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**PREDICTION OF BINARY VLE DATA  
THROUGH EQUATION OF STATE  
WITH WONG-SANDLER MIXING RULES**

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in Partial Fulfilment of the Requirements  
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*by*  
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*to the*  
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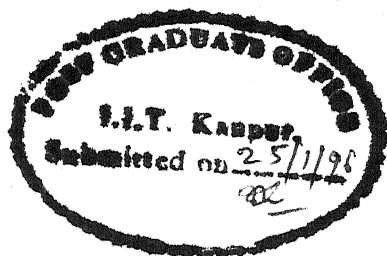
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## Abstract

The equation of state approach is being used widely for the prediction of phase equilibria, though this approach is suffering from the non availability of proper *mixing rules*.

By equating the calculated excess Helmholtz free energy from an equation of state to that from an activity coefficient model, a new mixing rule was developed. The use of the Helmholtz free energy makes it possible to satisfy the condition required by statistical mechanics (i.e. the second virial coefficient calculated from an equation of state should be a quadratic function of composition). Hence, the mixing rule produces the correct low - and high - density limits, without being density dependent.

In the present work, the new mixing rule is used for the prediction of vapor-liquid equilibria (VLE) of binary systems. The alcohols are polar in nature and hence they generally do not exhibit a regular behaviour and the commonly available mixing rules are unable to predict their phase equilibria satisfactorily. Hence, twenty binary systems containing alcohols or ethers as one of the components, are chosen to test the applicability of the new mixing rule for the prediction of VLE data. For this, bubble pressure calculations are carried out, by considering the experimental isothermal  $P$ - $X$  data. For ether-hydrocarbon systems, the Tsonopoulos  $K$  value has to be modified to a large extent. For the alcohol systems, the Tsonopoulos  $K$  value has to be modified, depending on the second component. Hence, the proposed Tsonopoulos  $K$  values are to be adjusted, in order to accurately predict the phase equilibria data by using the new mixing rule.

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## Notation

$B$	: Second virial coefficient
$D_y$	: Average absolute deviation in $y$
$D_p$	: Average absolute deviation in $P$
$K$	: Tsonopoulos binary interaction constant
$k$	: Binary interaction parameter
$N$	: Number of experimental points considered
$P$	: Pressure
$Q$	: Quadratic sum of the second virial coefficients
$R$	: Universal gas constant
$S$	: Entropy
$T$	: Temperature
$v$	: Molar volume
$\tilde{v}$	: partial molar volume
$x$	: Liquid composition, mole fraction
$X$	: Mole fraction vector
$y$	: Vapor composition, mole fraction

## Greek letters

$\alpha$	: NRTL model parameter
$\tau$	: NRTL model binary interaction parameter
$\phi$	: Fugacity coefficient
$\gamma$	: Activity coefficient

## Superscripts

$E$	: Excess property
$IG$	: Ideal gas
$IGM$	: Ideal gas mixture
$o$	: Reference state

## Subscripts

$i, j$	: Molecular species
$m$	: Mixture
$\infty$	: Infinite pressure state

# Chapter 1

## INTRODUCTION

Phase separation operations pose a challenging problem in chemical industries. Some of the most common separation processes employed in chemical industries are: *flash distillation, continuous column distillation, batch distillation, absorption, stripping, leaching, extraction ...etc.*

Among the various separation methods, distillation is the most important and widely used process, in which, the coexisting phases are vapor and liquid. Hence, reliable Vapor-Liquid Equilibria (VLE) data is of considerable importance in the design of distillation columns. For a large number of binary and for a few multi component systems the experimental VLE data can be found in literature [1]. However, the number of possible combinations of components of interest in chemical process design always far exceed the number of systems for which the experimental VLE data are available. This necessitates the designer either to experimentally determine or estimate the required VLE data.

The commonly used approaches, for phase equilibrium calculations, are the *activity coefficient approach* and the *equation of state approach*. The activity coefficient approach can be satisfactorily applied to predict the VLE data at low to moderate pressures. But, this method cannot be used at critical and super critical pressures. The equation of state approach is applicable over a wide range of pressures including critical and super critical pressures. However, the drawback associated with this approach is the inaccuracy of the existing mixing rules for mixtures. To model complex phase behaviour of highly nonideal mixtures, there are many proposals [2]-[4] to modify the van der Waals mixing rules which use composition-dependent binary interaction parameters. In the low-density limit these modified mixing rules are inconsistent with the statistical mechanical result that the second virial coefficient is a quadratic function of composition. To overcome this drawback, attempts have been made to develop density-dependent mixing rules [5]-[6], but with little success. An alternative approach for developing mixing rules was proposed by Huron and Vidal [7], by equating the excess Gibbs free energy at infinite pressure calculated from an

equation of state to that obtained from activity coefficient models for liquids. Even this proposal turned out to be inconsistent with the statistical mechanical result for the second virial coefficient.

In the present work, a new class of density-independent mixing rules are used. These are developed by considering the excess Helmholtz free energy, instead of Gibbs free energy. Using these mixing rules, the energy parameter  $a_m$  and the excluded volume parameter  $b_m$  of any cubic equation of state can be determined to give the correct excess Helmholtz energy at infinite pressure. In addition, these mixing rules lead to the correct quadratic composition dependence of the second virial coefficient. Hence, this new class of mixing rules produce results that are correct at both the low-density and high-density limits without being density dependent.

Several equations of state and the corresponding mixing rules are reviewed in Chapter 2. Chapter 3 presents the thermodynamics of phase equilibria and an expression to evaluate the fugacity coefficient of a component using the modified Peng-Robinson(PR) equation of state. The calculation procedure to predict VLE data and the relevant algorithm are presented in Chapter 4. The results are discussed in Chapter 5, while Chapter 6 deals with conclusions.

## Chapter 2

# EQUATIONS OF STATE AND MIXING RULES

An equation of state expresses a relationship between two or more thermodynamic properties. Although in principle functional relationships involving any three thermodynamic properties (For single-component, single-phase systems, the equation of state will always involve three properties) might be constructed, analytical expressions of the interrelationships among properties have been almost completely limited to  $P, T, v$ . Since pressure, volume and temperature can all be measured directly, the data needed to evaluate the constants in such equations can be obtained experimentally. An equation of state may be long and complicated, sometimes involving up to fifteen terms - as in the Martin-Hou equation [8] - or short and simple, with as few terms as the one term of the ideal gas equation. Till date several Equations Of State (EOS) have been proposed for the estimation of thermodynamic properties and only a few of them are in wide use.

### 2.1 Ideal Gas Equation Of State

Based on experimental data Sir Charles found that

$$PV = nRT \quad (2.1)$$

where  $R$  is the universal gas constant.

The value of  $R$  depends on the units of  $P$ ,  $V$ ,  $n$  and  $T$ . Equation (2.1) is a formal statement of the ideal gas equation of state. It is widely used for calculations involving gases and vapors at low pressures only, because as the pressure is increased, most gases no longer behave ideally.

## 2.2 van der Waals Equation Of State

In an effort to correct the ideal gas equation of state, which is based on two assumptions namely, infinitesimal molecular size and no intermolecular forces, van der Waals proposed the following functional relationship to describe the volumetric behaviour of fluids.

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \quad (2.2)$$

The term  $b$  is meant to account for the finite size of the gas molecules and is sometimes referred to as the *molecular volume*. Its value depends on the size and nature of gas molecules. The term  $\frac{a}{v^2}$  is a correction which is meant to account for the attractive forces that exist between molecules. The van der Waals equation is used, when a simple equation of state with somewhat greater accuracy than the ideal gas equation is desired.

It is possible to determine the parameters  $a$  and  $b$  of the van der Waals equation without recourse to specific  $P$ - $v$ - $T$  data from the following general observation. Experimental  $P$ - $v$  data on all real substances *at their critical temperature* indicates that the  $P$ - $v$  isotherm goes through a horizontal inflection point at the critical pressure of the substance. That is, both the first and second derivatives of  $P$  with respect to  $v$  vanish at the critical conditions.

$$\left(\frac{\partial P}{\partial v}\right)_T = \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0 \quad (2.3)$$

when  $P = P_c$  and  $T = T_c$ .

Substituting Equation (2.2) in Equation (2.3), we find that

$$a = \frac{27 R^2 T_c^2}{64 P_c} \quad (2.4)$$

$$b = \frac{RT_c}{8P_c} = \frac{v_c}{3} \quad (2.5)$$

## 2.3 Redlich-Kwong Equation Of State

The widely accepted two-constant equation of state is proposed by Redlich and Kwong [9] and is given by

$$P = \frac{RT}{(v - b)} - \frac{a}{T^{\frac{1}{2}}v(v + b)} \quad (2.6)$$

$$\text{where } a = 0.42748 \frac{R^2 T_c^{\frac{5}{2}}}{P_c}$$



$$\text{and } b = 0.08664 \frac{RT_c}{P_c}$$

The Redlich-Kwong equation is considered by many to be the best two-constant equation of state. However, for greater accuracy-particularly at high pressures and low temperatures-it is necessary to use more complex equations with a large number of constants.

## 2.4 Beattie-Bridgeman and Benedict-Webb-Rubin EOS

Among the more notable of the multiconstant EOS are those of Beattie-Bridgeman(B-B) [10] and Benedict-Webb-Rubin(B-W-R) [11]. The B-B equation of state is given by

$$Pv^2 = RT \left[ v + B_0 \left( 1 - \frac{b}{v} \right) \right] \left( 1 - \frac{c}{vT^3} \right) - A_0 \left( 1 - \frac{a}{v} \right) \quad (2.7)$$

The B-W-R equation of state is given by

$$P = \frac{RT}{v} + \frac{1}{v^2} \left( RT B_0 - A_0 - \frac{C_0}{T^2} \right) + \frac{1}{v^3} (RTb - a) + \frac{a\alpha}{v^6} + \frac{c}{T^2 v^3} \left( 1 + \frac{\gamma}{v^2} \right) \exp \left( \frac{-\gamma}{v^2} \right) \quad (2.8)$$

The B-B equation of state has five constants ( $A_0$ ,  $B_0$ ,  $a$ ,  $b$ , and  $c$ ) while the B-W-R equation of state has eight constants ( $A_0$ ,  $B_0$ ,  $C_0$ ,  $a$ ,  $b$ ,  $c$ ,  $\alpha$  and  $\gamma$ ). The B-B and B-W-R EOS may be used where the densities are less than 0.8 and 1.2 times the critical density, respectively.

The Redlich-Kwong, B-B and B-W-R EOS are of a semiempirical nature. That is, the form of these equations has generally been chosen such that they can accurately describe experimental data rather than conform to a theoretical description of actual molecular behaviour.

## 2.5 Virial Equation Of State

In 1901 Kamerlingh Onnes [12] suggested the virial equation of state:

$$Pv = RT + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \frac{D(T)}{v^3} \quad (2.9)$$

The parameters  $B(T)$ ,  $C(T)$ ,  $D(T)$ , ..... are called the *virial coefficients* which are functions of temperature only. The virial coefficients are directly related to the molecular forces that exist between groups of molecules. For example,  $B(T)$  describes interactions between pairs of molecules,  $C(T)$  describes interactions between groups of three molecules, and so on. These interactions are termed *virials* and may be expressed in terms of complicated integrals of the intermolecular forces. Thus, if one knows the intermolecular forces between any combination of molecules as functions of the molecular separations, it would be possible to perform the required integrations and obtain expressions for the virial coefficients without recourse to experimental data. But, these calculations are extremely complex and have not been successfully completed except for certain simplified intermolecular force potentials.

## 2.6 Soave Equation Of State

In 1972, Soave [13] proposed the following modification to the Redlich-Kwong equation of state.

$$P = \frac{RT}{(v - b)} - \frac{a(T)}{v(v + b)} \quad (2.10)$$

where

$$a(T) = a_{critical} \alpha(T)$$

$$a_{critical} = 0.42747 \frac{R^2 T_c^2}{P_c}$$

$$b = 0.08664 \frac{RT_c}{P_c}$$

The temperature dependence of the attractive term has been incorporated into the value of  $a$ .

To find  $\alpha(T)$ , Soave first derived the expression for the fugacity coefficient, then found values of  $\alpha$  which best represented the vapor pressures of various compounds. He found

$$\sqrt{\alpha} = 1 + k(1 - \sqrt{T_r}) \quad (2.11)$$

$$k = 0.480 + 1.574\omega - 0.176\omega^2 \quad (2.12)$$

where  $T_r$  is the reduced temperature and  $\omega$  is the acentric factor.

But, some of the pure component parameters used by Soave were inconsistent with those recommended in the *Technical Data Book: Petroleum Refining* [14]. Significant modifications to the Soave equation of state were made by Graboski and Daubert [15], Moysan and Paradowski [16] and Gibbons and Laughton [17].

## 2.7 Peng-Robinson Equation Of State

In 1976 Peng and Robinson [18] proposed an equation of state by extending some of the ideas presented by Soave. According to them

$$P = \frac{RT}{(v-b)} - \frac{a(T)}{v(v+b) + b(v-b)} \quad (2.13)$$

where

$$a = a_{critical}\alpha(T)$$

$$a_{critical} = 0.45724 \frac{R^2 T_c^2}{P_c}$$

$$\sqrt{\alpha} = 1 + k(1 - \sqrt{T_r})$$

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

$$b = 0.07780 \frac{RT_c}{P_c}$$

Stryjek and Vera [19] modified the Peng-Robinson equation of state, by introducing the parameter  $k_1$  which is specific for each compound, in the following way

$$P = \frac{RT}{(v-b)} - \frac{a(T)}{v^2 + 2bv - b^2} \quad (2.14)$$

where

$$a(T) = 0.457235 \frac{R^2 T_c^2}{P_c} \alpha(T)$$

$$\alpha(T) = [1 + k(1 - T_r^{0.5})]^2$$

$$k = k_0 + k_1(1 - T_r^{0.5})(0.7 - T_r)$$

$$k_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3$$

$$b = 0.077796 \left( \frac{RT_c}{P_c} \right)$$

## 2.8 Extension of Cubic EOS to Mixtures

The greatest utility of cubic EOS is for phase equilibrium calculations involving mixtures. The assumption inherent in such calculations is that the same equation of state used for pure fluids can be used for mixtures if we have a satisfactory way of obtaining the mixture parameters.

The application of a cubic, two parameter EOS to mixtures allows two degrees of freedom and hence one can choose the two mixture parameters to describe the behaviour of a mixture.

For relatively simple mixtures it is common to use the van der Waals one-fluid mixing rules [20] which are given by

$$b_{mix} = \sum_i \sum_j x_i x_j b_{ij} \quad (2.15)$$

$$a_{mix} = \sum_i \sum_j x_i x_j a_{ij} \quad (2.16)$$

along with the combining rules

$$b_{ij} = \frac{1}{2}(b_{ii} + b_{jj})(1 - l_{ij}) \quad (2.17)$$

$$a_{ij} = \sqrt{a_{ii}a_{jj}}(1 - k_{ij}) \quad (2.18)$$

Here  $a$  and  $b$  are the EOS parameters,  $x_i$  denotes mole fraction of component  $i$ ,  $k_{ij}$  and  $l_{ij}$  are binary interaction parameters. In the combining rule, generally  $l_{ij}$  is set equal to zero. With this approximation Equation (2.15) reduces to

$$b_{mix} = \sum_i x_i b_{ii} \quad (2.19)$$

Even with two binary parameters, the van der Waals mixing rules cannot accurately represent mixtures containing polar and associating compounds. Schwartzentruber et al. [3], Schwartzentruber and Renon [4] modified the van der Waals one-fluid mixing rules so that the properties of mixtures containing associating compounds can be predicted to a better accuracy.

Panagiotopoulos and Reid [2] proposed the following composition dependent binary interaction parameter

$$\delta_{ij} = k_{ij} - (k_{ij} - k_{ji})x_i \quad (2.20)$$

Since  $k_{ij} \neq k_{ji}$  there are two parameters for each binary pair. Michelsen and Kistenmacher [21] have shown that this mixing rule has significant shortcomings when applied to multicomponent systems. Some modifications have focused on ways to incorporate adjustable parameters which represent the intermolecular forces in much the same way activity coefficient models do-through the concept of local compositions.

In 1981, Heyen [22] introduced the local composition concept into the mixing rules in an attempt to account for non random mixing. He proposed the following equation to calculate the energy parameter  $a$ , in terms of  $x_j^{(i)}$  which is defined as the local mole fraction of species  $j$  around molecules of the local mole fraction of species  $i$ .

$$a = \sum_{i=1}^m x_i \sum_{j=1}^m x_j^{(i)} \sqrt{a_i a_j} (1 - \delta_{ij}) \quad (2.21)$$

where

$$x_j^{(i)} = \frac{x_j \tau_{ij}}{\sum_k x_k \tau_{ik}} \quad (2.22)$$

Heyen also introduced the following constraint on  $\tau_{ij}$ ,

$$\tau_{ij} \tau_{ji} = 1 \quad (2.23)$$

there by introducing only two adjustable parameters,  $\tau_{ij}$  and  $\delta_{ij}$ , per binary pair. For totally random mixtures  $\tau_{ij}$  is equal to one.

Let us now consider the mixing rules that combine excess free energy and equation of state models. The excess Gibbs free energy can be expressed as

$$\begin{aligned} \frac{G_{EOS}^{ex}(T, P, x_i)}{RT} &= \ln \phi_{mix}(T, P, x_i) - \sum_i x_i \ln \phi_i(T, P) \\ &= \left( Z_{mix}(T, P, x_i) - \sum_i x_i Z_i(T, P) \right) \\ &\quad - \left( \ln Z_{mix}(T, P, x_i) - \sum_i x_i \ln Z_i(T, P) \right) \\ &\quad - \left[ \int_{\infty}^{v_{mix}(T, P, x_i)} \frac{Z_{mix} - 1}{v_{mix}} dv - \sum_i x_i \int_{\infty}^{v_i(T, P)} \frac{Z_i - 1}{v_i} dv \right] \end{aligned} \quad (2.24)$$

Similarly the excess Helmholtz free energy of a mixture is given by

$$\begin{aligned} \frac{A_{EOS}^{ex}}{RT} &= - \left( \sum_i x_i \ln \frac{Z_{mix}(T, P, x_i)}{Z_i(T, P)} \right) \\ &\quad - \left[ \int_{\infty}^{v_{mix}(T, P, x_i)} \frac{Z - 1}{v} dv - \sum_i x_i \int_{\infty}^{v_i(T, P)} \frac{Z_i - 1}{v_i} dv \right] \end{aligned} \quad (2.25)$$

From the conventional definition of an excess property change on mixing, it is necessary that the pure components and the mixture be in the same state of aggregation to use these equations. It is obvious from these equations that the excess Gibbs free energy and the excess Helmholtz free energy of mixing computed from an equation of state depend on pressure, where as the excess functions obtained from activity coefficient models are independent of pressure or density. Therefore, the equality between  $G^{ex}$  (or  $A^{ex}$ ) obtained from equation of state models and activity coefficient models can be obtained at only a single pressure. The models that combine equations of state and activity coefficient models can be categorized into two groups as

- those that equate  $G^{ex}$ (or  $A^{ex}$ ) at infinite pressure.
- those that equate  $G^{ex}$ (or  $A^{ex}$ ) at low or zero pressure.

For the van der Waals type of cubic equations, the excess free energy functions are given by

$$\begin{aligned} \frac{G_{EOS}^{ex}}{RT} = & Z_{mix} - \sum_i x_i Z_i - \sum_i x_i \ln \frac{Z_{mix}}{Z_i} - \sum_i x_i \ln \left( \frac{1 - \frac{b_{mix}}{v_{mix}}}{1 - \frac{b_{ii}}{v_i}} \right) \\ & + \left( \frac{a_{mix}}{b_{mix} RT} \right) c(v_{mix}) - \sum_i x_i \left( \frac{a_{ii}}{b_{ii} RT} \right) \end{aligned} \quad (2.26)$$

$$\begin{aligned} \frac{A_{EOS}^{ex}}{RT} = & - \sum_i x_i \ln \frac{Z_{mix}}{Z_i} - \sum_i x_i \ln \left( \frac{1 - \frac{b_{mix}}{v_{mix}}}{1 - \frac{b_{ii}}{v_i}} \right) \\ & + \left( \frac{a_{mix}}{b_{mix} RT} \right) c(v_{mix}) - \sum_i x_i \left( \frac{a_{ii}}{b_{ii} RT} \right) \end{aligned} \quad (2.27)$$

Where  $c(v)$  is the molar volume dependent function which is specific for the chosen EOS.

For example for Peng-Robinson(PR) equation

$$c(v) = \frac{1}{2\sqrt{2}} \ln \left( \frac{v + (1 - \sqrt{2})b}{v + (1 + \sqrt{2})b} \right) \quad (2.28)$$

In the limit of infinite pressure, we find  $v_i \rightarrow b_{ii}$  and  $v_{mix} \rightarrow b_{mix}$  and  $c(v_{mix}=b_{mix}) = c(v_i=b_{ii}) = c^*$ ; Therefore for the PR equation

$$c^* = \frac{[\ln(\sqrt{2} - 1)]}{\sqrt{2}} = -0.62323 \quad (2.29)$$

$$\frac{A_{EOS}^{ex}(T, P \rightarrow \infty, x_i)}{c^* RT} = \frac{1}{RT} \left[ \frac{a_{mix}}{b_{mix}} - \sum_i x_i \frac{a_{ii}}{b_{ii}} \right] \quad (2.30)$$

$$\begin{aligned} \frac{G_{EOS}^{ex}(T, P \rightarrow \infty, x_i)}{c^* RT} = & \frac{1}{RT} \left[ \frac{a_{mix}}{b_{mix}} - \sum_i x_i \frac{a_{ii}}{b_{ii}} \right] \\ & + \frac{P}{RT} \sum_i x_i (b_{mix} - b_{ii}) \end{aligned} \quad (2.31)$$

## 2.9 Combination of Free Energy Models and EOS at Infinite Pressure

Huron and Vidal [7] made the first successful attempt of combining an equation of state and a free energy model. They equated the excess Gibbs free energy from an

equation of state to that obtained from an activity coefficient model  $G_\gamma^{ex}$  at infinite pressure (which uses one degree of freedom). From Equation (2.31) it is clear that for this to be true Equation (2.19) must be used (which uses the remaining one degree of freedom). Otherwise  $G_{EOS}^{ex}$  will be infinite at infinite pressure. The result of such an attempt give the following mixing rule

$$a_{mix} = b_{mix} \left[ \sum_i x_i \frac{a_{ii}}{b_{ii}} + \frac{G_\gamma^{ex}(T, x_i)}{c^*} \right] \quad (2.32)$$

$$b_{mix} = \sum_i x_i b_{ii} \quad (2.33)$$

The difficulties associated with this model are:

- Since  $G^{ex}$  is known experimentally to be a function of pressure, even at fixed temperature its value is not the same at low pressure and at infinite pressure. The  $G_\gamma^{ex}$  term in Equation (2.32) neglects this dependence. Hence the  $G_\gamma^{ex}$  parameters obtained at low pressures which are reported in compilations such as the DECHEMA Chemistry data series [1] cannot be used. Consequently data have to be recorrelated to use this model.
- The model parameters were found to be temperature sensitive. Therefore the model has little predictive capability.
- Since Equation (2.19) must be used, one cannot introduce the interaction parameter  $l_{ij}$  into the combining rule for the  $b$  parameter to improve phase and mixture density computations.
- Similarly, it is not possible to introduce an interaction parameter in the mixing rule to predict the parameter  $a$ .
- Finally, the mixing rule of Equation (2.33) does not satisfy the low density boundary condition which requires that the second virial coefficient is a quadratic function of composition as given below.

$$\begin{aligned} B_{mix}(T, x_i) &= \sum_i \sum_j x_i x_j B_{ij}(T) \\ &= \sum_i \sum_j x_i x_j \left( b_{ij} - \frac{a_{ij}}{RT} \right) = \left( b - \frac{a}{RT} \right)_{mix} \end{aligned} \quad (2.34)$$

Some researchers have argued that for the calculation of phase behaviour it is not necessary to satisfy the second virial coefficient boundary condition. However, the expression for the fugacity coefficient of a species in a mixture,  $\phi_i$ , needed for phase

behaviour calculations is computed from

$$\ln \phi_i = \ln \left( \frac{f_i}{x_i P} \right) + \frac{1}{RT} \int_{v=\infty}^{v_{mix}} \left[ \frac{RT}{v} - \left( \frac{\partial P}{\partial n_i} \right)_{T,v,N_{j \neq i}} \right] dv - \ln Z \quad (2.35)$$

From this integral, it is evident that the composition dependence of the pressure at all densities affects the fugacity coefficient at any density. The fact that violation of a known boundary condition is theoretically inconsistent and this becomes a potential source of error in phase behaviour calculations.

The Wong-Sandler(WS) mixing rule [23] is also based on the idea of equating free energies at infinite pressure, but makes use of the excess Helmholtz free energy. This has the following two important advantages:

- Since Equation (2.30) is used rather than Equation (2.31), one does not have to use the remaining degree of freedom in the choice of mixture parameters because one can make the assumption that the excess volume of mixing at infinite pressure is zero.
- The excess Helmholtz free energy of mixing of a liquid is much less sensitive function of pressure than the excess Gibbs free energy of mixing. Therefore, to a reasonable approximation we can write

$$\begin{aligned} A_\gamma^{ex}(T, P = \infty, x_i) &\approx A_\gamma^{ex}(T, P^*, x_i) \\ &= G_\gamma^{ex}(T, P^*, x_i) - P^* v_{ex}(T, P^*, x_i) \\ &\approx G_\gamma^{ex}(T, P^*, x_i) \end{aligned} \quad (2.36)$$

Where  $P^*$  is any low pressure at which experimental data are available. Hence the last equality in Equation (2.36) is valid if this pressure is low. Even after using Equation (2.30) and Equation (2.36), Wong-Sandler are left with one degree of freedom. Out of the several possibilities for this additional specification, they chose to satisfy the composition dependence of the second virial coefficient as given by Equation (2.34). By adopting the above arguments they obtained the following mixing rules.

$$a_{mix} = \frac{\sum_i \sum_j x_i x_j \left( b_{ij} - \frac{a_{ij}}{RT} \right) \left[ \sum_i x_i \frac{a_i}{b_i} + \frac{G_\gamma^{ex}(T, P^*, x_i)}{C^*} \right]}{RT - \left[ \sum_i x_i \frac{a_i}{b_i} + \frac{G_\gamma^{ex}(T, P^*, x_i)}{C^*} \right]} \quad (2.37)$$

$$b_{mix} = \frac{\sum_i \sum_j x_i x_j \left( b_{ij} - \frac{a_{ij}}{RT} \right)}{RT - \left[ \sum_i x_i \frac{a_i}{b_i} + \frac{G_\gamma^{ex}(T, P^*, x_i)}{C^*} \right]} \quad (2.38)$$

The advantages of the above mixing rules are:



- They satisfy the two known boundary conditions -

- (a) At low pressures the equation of state should produce a second virial coefficient that is quadratic in composition.
  - (b) At high densities the equation of state should behave like an activity coefficient model. These are satisfied even though the mixing rules are themselves density independent.
- Since the excess Gibbs free energy model is used at the pressure of the measurements, a reevaluation of parameters is not needed.
- The model also has the additional flexibility of adding binary interaction parameters. These can be introduced in the form

$$\left[ b_{ij} - \frac{a_{ij}}{RT} \right] = \frac{1}{2} \left[ \left( b_{ii} - \frac{a_{ii}}{RT} \right) + \left( b_{jj} - \frac{a_{jj}}{RT} \right) \right] (1 - k_{ij}) \quad (2.39)$$

Regarding the importance of the value of  $k_{ij}$ , it is not true that

$$\begin{aligned} A_{EOS}^{ex}(T, P = \infty, x_i) &\approx A_{EOS}^{ex}(T, P^*, x_i) \\ &= G_{EOS}^{ex}(T, P^*, x_i) - P^* v_{ex}(T, P^*, x_i) \\ &\approx G_{EOS}^{ex}(T, P^*, x_i) \end{aligned} \quad (2.40)$$

for any arbitrary value of  $k_{ij}$ . Therefore, the binary interaction parameter  $k_{ij}$  should be chosen such that either  $A_{EOS}^{ex}$  is essentially independent of pressure or the experimental  $G_{EOS}^{ex}$  curve is reproduced as closely as possible at the pressure of the measurements. Thus the parameter  $k_{ij}$  contains no further information than that already included in  $G_{EOS}^{ex}$ .

## 2.10 Combination of Free Energy Models and EOS at Low or Zero Pressure

While developing the UNIWAALS equation, Gupte et al. [24] used the combination of Equation (2.15) and Equation (2.27) at the experimental pressure to obtain the UNIWAALS model. This approach does not satisfy the second virial coefficient boundary condition, and requires one to solve for the liquid density from the volumetric equation of state three times for a given mixture for each of the two pure components, and for the mixture. A complication that arises in this method is that there may not be a liquid density solution for one or more of the pure components at the temperature and pressure of the mixture. This either restricts the method to mixtures in which all pure components are liquids at the temperature and pressure of interest or requires some sort of extrapolation technique. Further, there is an inconsistency in the method in

that the resulting mixture equation of state parameters are implicit functions of pressure (or density). Consequently, when applying the same equation of state to both the pure fluids and the mixture, the volumetric dependence on the equation of state for the mixture is different from that for the pure fluids due to the implicit pressure dependence of the mixture parameters. Gani et al. [25] eliminated some of these problems with the UNIWAALS model. However, the computational aspects of the resultant model are still too complex for routine use.

The only mixing rules that combine EOS and activity coefficient models which are free of ad hoc assumptions are those that equate  $G^{ex}$  (or  $A^{ex}$ ) at infinite pressure. None the less, all the models mentioned above can be useful for predictions and correlations at some conditions, though inconsistencies may arise at other conditions.

## Chapter 3

# VLE-PR EQUATION OF STATE WITH WONG-SANDLER MIXING RULES

### 3.1 Thermodynamic Relationships

The internal energy of a closed, homogeneous system can be expressed as

$$dU = TdS - PdV \quad (3.1)$$

where  $U$  is the internal energy,  
 $S$  is the entropy,  
and  $V$  is the volume.

For a system to be at equilibrium, the internal energy must be at a minimum. That is,

$$dU_{S,V} = 0 \quad (3.2)$$

Calculation of internal energy using Equation (3.1) requires a knowledge of expressions explicit in entropy and volume to integrate the terms on the right hand side of Equation (3.1). Rearrangement of Equation (3.1) enables the use of temperature explicit or pressure explicit expressions in the calculation of energy. For example, suppose that one has available an expression which accurately represents the pressure of a system over the conditions of interest. This expression can be used in the calculation of energy changes if the enthalpy,  $H$ , is defined as

$$H = U + PV \quad (3.3)$$

Differentiating Equation (3.3) and substituting from Equation (3.1), we get

$$dH = TdS + VdP \quad (3.4)$$

To use temperature explicit and volume explicit expressions in the calculation of energy, the Helmholtz energy,  $A$ , is defined as

$$A = U - TS \quad (3.5)$$

From Equation (3.1) and Equation (3.5) one can obtain

$$dA = -SdT - PdV \quad (3.6)$$

Equation (3.1) can also be rearranged so that the calculation of energy is made using expressions explicit in temperature and pressure. The rearrangement is as follows

$$G = H - TS \quad (3.7)$$

where  $G$  is the Gibbs free energy.

From Equations (3.4) and (3.7) one can get

$$dG = -SdT + VdP \quad (3.8)$$

for a system to be in a state of equilibrium at constant temperature and pressure. That is the excess Gibbs energy must be at a minimum.

$$dG_{T,P} = 0 \quad (3.9)$$

## 3.2 Chemical Potential

Equations (3.1), (3.4), (3.6) and (3.8) are valid only for systems with a single component. For systems of two or more components, the internal energy becomes a function of the number of moles of each component present. That is

$$U = f(S, V, n_1, n_2 \dots n_m) \quad (3.10)$$

The chemical potential is defined as

$$\mu_i = \left[ \frac{\partial U}{\partial n_i} \right]_{S,V,n_j} \quad (3.11)$$

Then Equation (3.1) becomes

$$dU = TdS - PdV + \sum \mu_i dn_i \quad (3.12)$$

where  $\mu_i$  is the chemical potential of component  $i$ .

Similarly

$$dG = -SdT + VdP + \sum \mu_i dn_i \quad (3.13)$$

and

$$\mu_i = \left[ \frac{\partial G}{\partial n_i} \right]_{T,P,n_j} \quad (3.14)$$

The partial differential appearing in Equation (3.14) is the partial molar Gibbs energy. This relationship is important in the development of the activity coefficient.

When a closed, heterogeneous system is at equilibrium, these potentials, (or intensive properties), are equal for each component in each phase. If a system of  $m$  components has vapor and liquid phases in equilibrium, the following relationships hold

$$T^v = T^l \quad (3.15)$$

$$P^v = P^l \quad (3.16)$$

$$\mu_1^v = \mu_1^l \quad (3.17)$$

$$\cdot \quad \cdot$$

$$\cdot \quad \cdot$$

$$\cdot \quad \cdot$$

$$\cdot \quad \cdot$$

$$\mu_m^v = \mu_m^l \quad (3.18)$$

### 3.3 Fugacity and Fugacity Coefficient

The practical convenience dictates that the thermodynamic relationships for a system must be expressed in terms of quantities that can be measured experimentally. In the case of the phase equilibrium conditions, the temperature and pressure can be directly measured, where as the chemical potential can be expressed in terms of experimentally accessible quantities. By differentiating Equation (3.7) and combining the result with the first and second laws of thermodynamics one obtains

$$d\mu_i = -s_i dT + v_i dP \quad (3.19)$$

$$\left[ \frac{\partial \mu_i}{\partial P} \right]_T = v_i \quad (3.20)$$

In the case of an ideal gas,

$$v_i = \frac{RT}{P} \quad (3.21)$$

Substituting Equation (3.21) in Equation (3.19) and integrating Equation (3.19) at constant temperature yields

$$\mu_i - \mu_i^0 = RT \ln \frac{P}{P^0} \quad (3.22)$$

where the superscript 0 signifies a reference state for the quantity.

The chemical potential cannot be calculated directly. But, one can evaluate the change in the chemical potential of an ideal gas when the pressure changes from some reference value  $P^0$  to the pressure  $P$ . Equation (3.22) is valid only for an ideal gas. To extend the relationship given by Equation (3.22) to real systems which are not ideal gases, G.N.Lewis defined a function  $f$  called the fugacity

$$\mu_i - \mu_i^0 = RT \ln \frac{f_i}{f_i^0} \quad (3.23)$$

For ideal gases, the fugacity is equal to the pressure, and for mixtures of ideal gases, the fugacity is equal to the partial pressure. The fugacity is often referred to as a *corrected pressure*. If one considers two phases  $\alpha$  and  $\beta$  in equilibrium, the criterion for equilibrium gives

$$\mu_i^{0\alpha} = \mu_i^{0\beta} \quad (3.24)$$

$$f_i^{0\alpha} = f_i^{0\beta} \quad (3.25)$$

$$f_i^\alpha = f_i^\beta \quad (3.26)$$

Equation (3.26) is a restatement of the equilibrium conditions expressed in Equation (3.17). The fugacity then replaces the chemical potential as the criterion for equilibrium. It is through the fugacity that the conditions of equilibrium will be expressed in terms of the experimental quantities of pressure, temperature, volume and concentration.

The fugacity coefficient of component  $i$ ,  $\phi_i$  is defined as

$$\phi_i = \frac{f_i}{y_i P} \quad (3.27)$$

For an ideal gas the fugacity coefficient is equal to unity. The greater the fugacity coefficient deviates from unity, the system deviates greater from ideal behaviour.

The approaches commonly used in expressing the equality of the fugacities in vapor-liquid equilibrium are

- The equation of state approach.
- The activity coefficient approach.

### 3.4 Equation Of State Approach

The fugacity of a component  $i$  in a mixture is given by

$$RT \ln \phi_i = RT \ln \frac{f_i}{y_i P} = \int_0^P \left[ \tilde{v}_i - \frac{RT}{P} \right] dP \quad (3.28)$$

where

$$\tilde{v}_i = \left[ \frac{\partial V}{\partial n_i} \right]_{T,P,n_j} \quad (3.29)$$

For pure components, the partial molar volume  $\tilde{v}_i$  is equal to the molar volume  $v_i$ , and the Equation (3.28) reduces to

$$RT \ln \frac{f}{P} = \int_0^P \left[ v_i - \frac{RT}{P} \right] dP \quad (3.30)$$

But, explicit representation of volume by an equation of state is often difficult. A better alternative is to characterize the system with a pressure explicit equation of state. For a given volume and temperature, the system can exist at only one pressure. In contrast, volume is not a unique function of temperature, pressure and concentration.

For a pressure explicit equation of state, the fugacity coefficient is given by

$$RT \ln \phi_i = RT \ln \frac{f_i}{y_i P} = \int_{V^*}^{\infty} \left[ \left( \frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V^*} \right] dV^* - RT \ln Z \quad (3.31)$$

where  $Z$  is the compressibility factor which is defined as

$$Z = \frac{PV^*}{RT} \quad (3.32)$$

Equation (3.26) requires that for vapor-liquid equilibrium the fugacity of a component in the vapor phase must be equal to the fugacity of the same component in the liquid phase. Substituting Equation (3.27) into Equation (3.26) results

$$y_i P \phi_i^v = x_i P \phi_i^l \quad (3.33)$$

$$y_i \phi_i^v = x_i \phi_i^l \quad (3.34)$$

For a binary system, the equilibrium constraints are

$$y_1 \phi_1^v = x_1 \phi_1^l \quad (3.35)$$

$$y_2 \phi_2^v = x_2 \phi_2^l \quad (3.36)$$

A typical VLE data set for a binary system consists of the pressure, temperature, and liquid and vapor compositions. With an accurate equation of state to represent the volumetric behaviour of the system, one needs only information about two of the measured quantities, and one can solve the system of Equations (3.35) and (3.36) to obtain the other two quantities. For example, knowing the pressure and liquid compositions, the system of Equations (3.35) and (3.36) can be solved for the equilibrium temperature and pressure.

### 3.5 Activity Coefficient Approach

Equation (3.31) requires an integration from the volume (or density) of interest to infinite volume (or to density of zero). For an equation of state to be accurate in liquid phase, it must be accurate from this implied ideal gas state to the dense liquid state. Unfortunately, the accuracy of many equations of state breaks down considerably at high densities. Because of this deficiency, a different approach is often used to describe the fugacity of the liquid phase. The basis of this approach is the *activity*, defined as

$$a_i = \frac{f_i(T, P, x_i)}{f_i^0(T, P, x_i^0)} \quad (3.37)$$

Here  $a_i$  is the activity of component  $i$  and  $f_i^0$  is the standard state fugacity (at some arbitrarily defined pressure,  $P^0$ , and some arbitrarily defined composition  $x_i^0$ ). The activity coefficient,  $\gamma_i$ , is defined as

$$\gamma_i = \frac{a_i}{x_i} = \frac{f_i}{x_i f_i^0} \quad (3.38)$$

Then the equilibrium constraints become

$$f_i^l = \gamma_i x_i f_i^0 \quad (3.39)$$

$$y_i P \phi_i^v = \gamma_i x_i f_i^0 \quad (3.40)$$

### 3.6 Derivation of the Expression for Fugacity Coefficient

The modified Peng-Robinson equation of state is given by

$$P = \frac{RT}{v - b} - \frac{a}{v^2 + 2bv - b^2} \quad (3.41)$$

where

$$a = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha$$

$$\alpha = \left[ 1 + k(1 - \sqrt{T_r}) \right]^2$$

$$k = k_0 + k_1(1 + T_r^{0.5})(0.7 - T_r)$$

$$k_0 = 0.378893 + 1.4897153\omega - 0.1713848\omega^2 + 0.0196554\omega^3$$

$$b = 0.077796 \frac{RT_c}{P_c}$$



To apply this equation to mixtures, the equation of state parameters  $a_m$  and  $b_m$  are to be made functions of compositions using mixing rules. If the compressibility factor  $\frac{Pv}{RT}$  is expanded in a virial series, the expression for the second virial coefficient is

$$B(T) = b - \frac{a}{RT} \quad (3.42)$$

Since, from statistical mechanics, the composition dependence of the second virial coefficient is quadratic and is given by

$$B_m(T) = \sum_i \sum_j x_i x_j B_{ij}(T) \quad (3.43)$$

$$b_m - \frac{a_m}{RT} = \sum_i \sum_j x_i x_j \left( b - \frac{a}{RT} \right)_{ij} \quad (3.44)$$

Where  $\left( b - \frac{a}{RT} \right)_{ij}$  is the composition-independent cross second virial coefficient of the equation of state.

The Helmholtz free energy departure function for the Peng-Robinson equation of state at a given temperature, pressure and composition is given by

$$\frac{(A - A^{IGM})}{RT} = -\ln \left[ \frac{P(v - b)}{RT} \right] + \frac{a}{2\sqrt{2}bRT} \ln \left[ \frac{v + (1 - \sqrt{2})b}{v + (1 + \sqrt{2})b} \right] \quad (3.45)$$

In the limit of pressure going to infinity

$$\lim_{P \rightarrow \infty} \frac{A - A^{IGM}}{RT} = \frac{a}{bRT} c \quad (3.46)$$

$$\text{Where } c = \frac{1}{\sqrt{2}} \ln(\sqrt{2} - 1).$$

Therefore, the excess Helmholtz free energy at infinite pressure is given by

$$\frac{A_\infty^E}{cRT} = \frac{a_m}{b_m RT} - \sum_i x_i \frac{a_i}{b_i RT} \quad (3.47)$$

From Equations(3.4) and (3.7) one can obtain

$$b_m = \frac{Q}{1 - D} \quad (3.48)$$

and

$$a_m = Q \frac{D}{1 - D} \quad (3.49)$$

Where Q and D are defined as

$$Q = \sum_i \sum_j x_i x_j \left( b - \frac{a}{RT} \right)_{ij} \quad (3.50)$$

$$D = \sum_i x_i \frac{a_i}{b_i RT} + \frac{A_\infty^E}{cRT} \quad (3.51)$$

The fugacity coefficient is computed from

$$\ln \phi_i = \int_v^\infty \left[ \frac{1}{RT} \left( \frac{\partial P}{\partial n_i} \right)_{T,v,n_j} - \frac{1}{v} \right] dv - \ln \left( \frac{Pv}{RT} \right) \quad (3.52)$$

For the Peng-Robinson equation of state with an arbitrary set of mixing rules for  $a_m$  and  $b_m$ , one obtains

$$\begin{aligned} \ln \phi_i = & -\ln \left[ \frac{P(v - b_m)}{RT} \right] + \frac{1}{b_m} \left( \frac{\partial n b_m}{\partial n_i} \right) \left( \frac{Pv}{RT} - 1 \right) \\ & + \frac{1}{2\sqrt{2}} \left( \frac{a_m}{b_m RT} \right) \left[ \frac{1}{a_m} \left( \frac{1}{n} \frac{\partial n^2 a_m}{\partial n_i} \right) - \frac{1}{b_m} \left( \frac{\partial n b_m}{\partial n_i} \right) \right] \ln \left[ \frac{v + b_m(1 - \sqrt{2})}{v + b_m(1 + \sqrt{2})} \right] \end{aligned} \quad (3.53)$$

Where the partial derivatives of  $a_m$  and  $b_m$  are given by

$$\frac{\partial n b_m}{\partial n_i} = \frac{1}{1 - D} \left( \frac{1}{n} \frac{\partial n^2 Q}{\partial n_i} \right) - \frac{Q}{(1 - D)^2} \left( 1 - \frac{\partial n D}{\partial n_i} \right) \quad (3.54)$$

and

$$\frac{1}{RT} \left( \frac{1}{n} \frac{\partial n^2 a_m}{\partial n_i} \right) = D \frac{\partial n b_m}{\partial n_i} + b_m \frac{\partial n D}{\partial n_i} \quad (3.55)$$

with the partial derivatives of Q and D given by

$$\left( \frac{1}{n} \frac{\partial n^2 Q}{\partial n_i} \right) = 2 \sum_j x_j \left( b - \frac{a}{RT} \right)_{ij} \quad (3.56)$$

$$\frac{\partial n D}{\partial n_i} = \frac{a_i}{b_i RT} + \frac{\ln \gamma_{\infty i}}{c} \quad (3.57)$$

with

$$\ln \gamma_{\infty i} = \frac{1}{RT} \frac{\partial n A_\infty^E}{\partial n_i} \quad (3.58)$$

The NRTL(Non-Random Two Liquid) model gives

$$\frac{A_\infty^E}{RT} = \sum_i x_i \left[ \frac{\sum_j x_j \tau_{ji} g_{ji}}{\sum_k x_k g_{ki}} \right] \quad (3.59)$$

where

$$\begin{aligned} g_{ij} &= \exp(-\alpha_{ij} \tau_{ij}) \\ \tau_{ji} &= \frac{g_{ji} - g_{ii}}{RT} \\ \alpha_{ji} &= \alpha_{ij} \end{aligned}$$

by substituting Equation (3.59) in Equation (3.58), we obtain

$$\ln \gamma_{\infty i} = \frac{\sum_j x_j \tau_{ji} g_{ji}}{\sum_k x_k g_{ki}} + \sum_j \frac{x_j g_{ij}}{\sum_k x_k g_{kj}} \left( \tau_{ij} - \frac{\sum_l x_l \tau_{lj} g_{lj}}{\sum_k x_k g_{kj}} \right) \quad (3.60)$$

### 3.7 Cross Second Virial Coefficient

The second virial coefficient from the equation of state is given by [see Equation (3.42)]

$$B(T) = b - \frac{a}{RT} \quad (3.61)$$

for a binary system, we can write

$$B_{11} = b_{11} - \frac{a_{11}}{RT} \quad (3.62)$$

$$B_{22} = b_{22} - \frac{a_{22}}{RT} \quad (3.63)$$

In order to evaluate the cross-second virial coefficient  $B_{12}$ , one can use the relation

$$B_{12}^{EOS} = \frac{(B_{11}^{EOS} + B_{22}^{EOS})}{2}(1 - k_{12}) \quad (3.64)$$

where the value of  $k_{12}$  is obtained by the following procedure.

- \*  $B_{12}^{EOS}/B_{12}^{EXP}$  cross temperature is evaluated by using  $T_{r,12} = 0.84$  and Tsonopoulos  $K_{12}$  value in

$$T_{r,12} = \frac{\hat{T}}{T_{c,12}} \quad (3.65)$$

and

$$T_{c,12} = \sqrt{T_{c,1}T_{c,2}}(1 - K_{12}) \quad (3.66)$$

- \* At the cross temperature  $\hat{T}$ ,  $\hat{B}_{11}$ ,  $\hat{B}_{22}$  and  $\hat{B}_{12}$  are evaluated using

$$\hat{B}_{11} = b_{11} - \frac{a_{11}}{R\hat{T}} \quad (3.67)$$

$$\hat{B}_{22} = b_{22} - \frac{a_{22}}{R\hat{T}} \quad (3.68)$$

$$\hat{B}_{12} = \frac{RT_c}{P_c}(f_0 + \omega f_1) \quad (3.69)$$

where

$$T_{c,12} = \sqrt{T_{c,1}T_{c,2}}(1 - K_{12})$$

$$P_{c,12} = \frac{4T_{c,12} \left[ \left( \frac{P_{c,1}v_{c,1}}{T_{c,1}} \right) + \left( \frac{P_{c,2}v_{c,2}}{T_{c,2}} \right) \right]}{\left[ (v_{c,1})^{\frac{1}{3}} + (v_{c,2})^{\frac{1}{3}} \right]^3}$$

$$\omega_{12} = \frac{(\omega_1 + \omega_2)}{2}$$

$$f_0 = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} - \frac{0.000607}{T_r^4}$$

$$f_1 = 0.073 - \frac{0.460}{T_r} - \frac{0.50}{T_r^2} - \frac{0.097}{T_r^3} - \frac{0.0073}{T_r^4}$$

\* Using  $\hat{\theta}_{11}$ ,  $\hat{\theta}_{22}$ , and  $\hat{\theta}_{12}$  the value of  $k_{12}$  is obtained from

$$k_{12} = 1 - 2 \frac{\hat{\theta}_{12}}{(\hat{\theta}_{11} + \hat{\theta}_{22})} \quad (3.70)$$

\* Using the value of  $k_{12}$  in Equation (3.64)  $B_{12}^{EOS}$  is calculated at all temperatures.

# Chapter 4

## VLE CALCULATION AND ALGORITHM

### 4.1 The General VLE Problem

In general VLE problems are classified into four types. They are

BUBL  $P$  : calculate  $y$  and  $P$ , given  $x$  and  $T$

DEW  $P$  : calculate  $x$  and  $P$ , given  $y$  and  $T$

BUBL  $T$  : calculate  $y$  and  $T$ , given  $x$  and  $P$

DEW  $T$  : calculate  $x$  and  $T$ , given  $y$  and  $P$

The number of intensive parameters which must be specified to fix unambiguously the state of equilibrium is given by the Gibb's rule as:

$$\begin{array}{l} \text{Number of independent} = \text{Number of components} \\ \text{intensive variables} \quad \quad - \text{Number of phases} + 2 \end{array}$$

Thus, for a  $n$  component two phase system, one specifies either  $T$  or  $P$  and either the liquid phase or the vapor phase composition. In other words  $1+(n-1)$  variables are specified. Then the total number of variables to be determined are  $n+2$ . Hence the following  $n+2$  equations are necessary to determine these  $n+2$  variables.

- $n$  equilibrium relationships for  $n$  components
- An equation of state for vapor phase and
- An equation of state for liquid phase.

Since all the  $n + 2$  variables are involved implicitly in these equations, iterative procedure is used to determine these variables.

A flowchart for bubble pressure calculation is presented in Fig. [4.1].

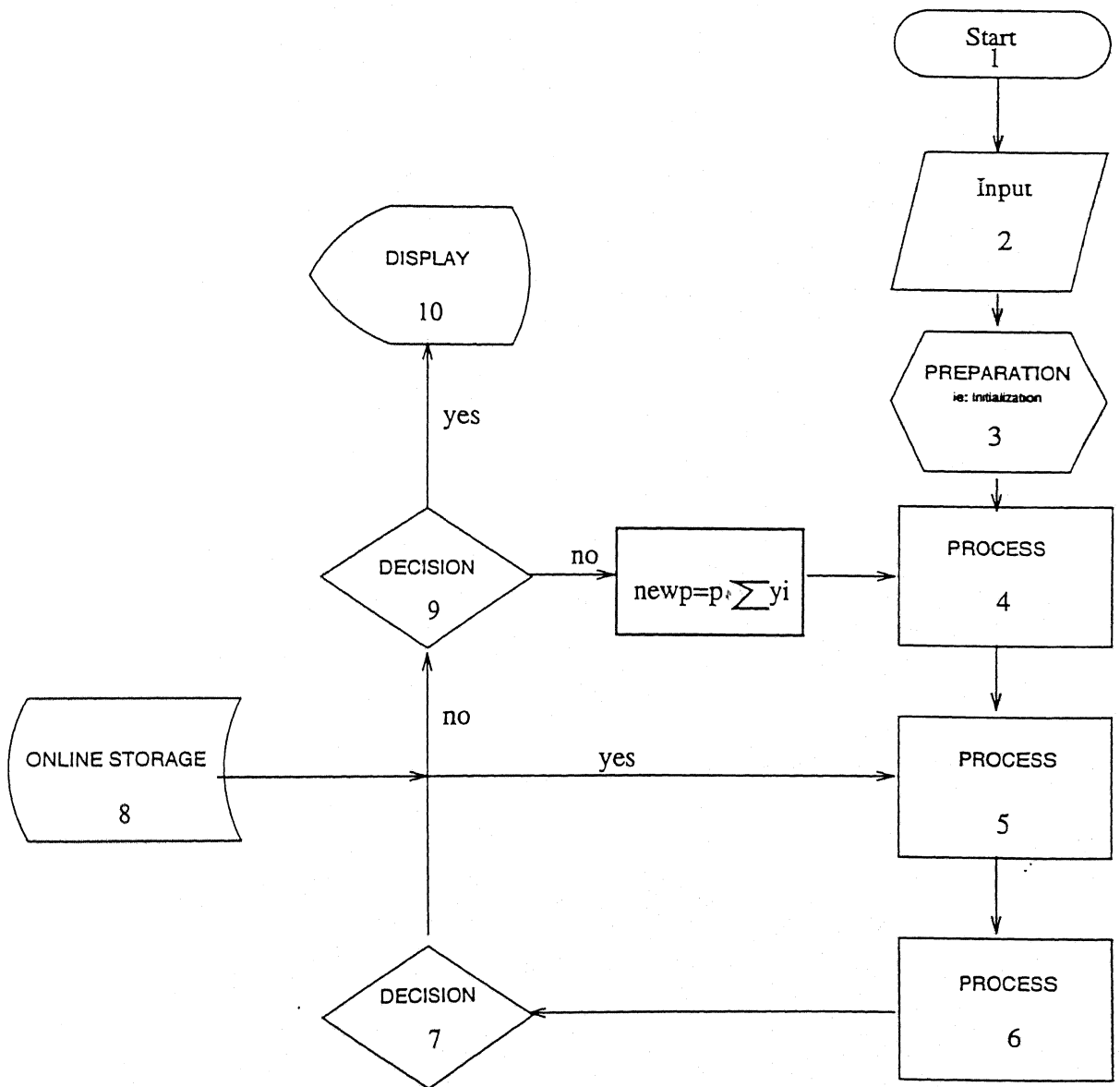


Figure 4.1: Flowchart for BUBBLE P calculation

## 4.2 Calculation Procedure

The calculation procedure with reference to the box numbers of Fig. [4.1] is presented below.

- \* Box.2-Read the values of physical property data necessary for the evaluation of all equation of state parameters. Read the experimental values of temperature and liquid composition
- \* Box.3-Initialize pressure and vapor composition
- \* Box.4-Evaluate  $\phi_i^l$
- \* Box.5-Evaluate  $\phi_i^v$  and  $K_i$
- \* Box.6-Evaluate new vapor composition  $y_i = K_i x_i$
- \* Box.7-If summation of  $y_i$  is not changing, go to step 9 (or box.9). Else, repeat the steps 5 and 6. (or boxes 5 and 6).
- \* Box.8-On line storage retains the values of  $\phi_i^l$
- \* Box.9-If  $\sum_i y_i = 1$ , then print bubble pressure and vapor composition. Else change the pressure and repeat the procedure from step 4. (or box.4)



## Chapter 5

# RESULTS AND DISCUSSION

The modified Peng-Robinson equation of state (Stryjek and Vera [19]) with new mixing rules (Wong and Sandler [23]) has been used to study the VLE of twenty binary systems. These systems contain either alcohol or ether as one of the components. Generally, the polar systems do not exhibit a regular behaviour and the commonly available mixing rules cannot be employed to study their phase equilibria, because of the poor applicability of the common mixing rules to polar systems. As the new mixing rules have a sound theoretical base, these can be used to study the phase behaviour of complex systems with much confidence. To get the correct pure component vapor pressures, the equation of state constants for the pure components are computed using the correlation of Stryjek and Vera [19]. Since several excess free energy models are available to describe the phase behaviour one can choose any of the available models. In this work the NRTL model is used.

BUBL  $P$  computations are carried out, for twenty binary systems. Five of the twenty systems are chosen as reference systems. For these reference systems, the results are compared for different binary interaction parameter values, in Tables [5.1-5.5]. For the rest of the systems, the results are presented for the best binary interaction parameter value and for the Tsonopoulos constant value in Tables [5.6-5.20]. The average absolute deviation in pressure as well as in vapor composition are presented in Tables [5.1-5.20]. The results are elucidated in Figures [5.1-5.20]. The results are in very good agreement with experimental values, except for alcohol-halogenated hydrocarbon systems. For ether-hydrocarbon systems, the results are in good agreement, for Tsonopoulos binary interaction value of zero. For alcohol systems, the proposed Tsonopoulos binary interaction constant is tuned depending on the second component of the system.

Table 5.1: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *acetone – ethanol* system at 313.15 K.

$x_1$	$y_1(exp)$	$P(exp)$	$K=0.050$		$K=0.030$		$K=0.100$		$K=0.000$	
			$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$
0.0250	0.1435	0.20285	0.1492	0.20698	0.1409	0.20285	0.1741	0.21320	0.1249	0.20285
0.0500	0.2460	0.22457	0.2555	0.23101	0.2440	0.22457	0.2904	0.24239	0.2213	0.22080
0.0750	0.3205	0.24430	0.3352	0.25277	0.3197	0.24696	0.3737	0.26839	0.2966	0.23872
0.1000	0.3795	0.26309	0.3973	0.27253	0.3848	0.26309	0.4363	0.29159	0.3576	0.25536
0.1500	0.4700	0.29761	0.4884	0.30704	0.4745	0.29761	0.5243	0.33096	0.4515	0.28533
0.2000	0.5380	0.32640	0.5529	0.33612	0.5397	0.32640	0.5837	0.36277	0.5211	0.31168
0.2500	0.5900	0.35172	0.6017	0.36100	0.5893	0.35172	0.6269	0.38883	0.5758	0.33520
0.3000	0.6310	0.37398	0.6408	0.38267	0.6295	0.37398	0.6604	0.41053	0.6208	0.35650
0.8000	0.8930	0.52379	0.8941	0.52379	0.8917	0.52379	0.8770	0.53750	0.9002	0.51634
0.9000	0.9450	0.54564	0.9488	0.54564	0.9482	0.54564	0.9325	0.55617	0.9472	0.54564
$D_y^1$			0.0107		0.0024		0.0380		0.0158	
$DP^2$				0.00656		0.00026		0.02484		0.00855

$$^1D_y = \frac{\sum |y(cal) - y(exp)|}{N}$$

$$^2D_P = \frac{\sum |P(cal) - P(exp)|}{N}$$

Table 5.2: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *benzene* – 1,4 – *dioxane* system at 298.15 K.

$x_1$	$y_1(exp)$	$P(exp)$	$K=0.000$		$K=0.010$		$K=0.050$		$K=0.150$	
			$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$
0.0000	0.0000	0.04891	0.0000	0.05181	0.0000	0.05181	0.0000	0.05181	0.0000	0.05181
0.0626	0.1507	0.05597	0.1502	0.05718	0.1918	0.06018	0.1705	0.05861	0.2138	0.06188
0.1456	0.3112	0.06250	0.3084	0.06414	0.3642	0.07014	0.3361	0.06701	0.3925	0.07354
0.2946	0.5241	0.07450	0.5159	0.07612	0.5553	0.08499	0.5356	0.08041	0.5749	0.08986
0.4687	0.6969	0.08743	0.6844	0.08927	0.6917	0.09826	0.6880	0.09370	0.6954	0.10294
0.5609	0.7673	0.09436	0.7540	0.09587	0.7472	0.10399	0.7507	0.09990	0.7436	0.10813
0.6203	0.8069	0.09942	0.7986	0.09942	0.7801	0.10735	0.7872	0.10366	0.7728	0.11107
0.7573	0.8857	0.11022	0.8674	0.11022	0.8536	0.11435	0.8648	0.11176	0.8416	0.11700
0.8258	0.9201	0.11515	0.9121	0.11368	0.8914	0.11754	0.9055	0.11515	0.8797	0.11959
1.0000	1.0000	0.12581	0.9918	0.12581	0.9918	0.12581	0.9918	0.12581	0.9918	0.12581
$D_y$			0.0080		0.0246		0.0145		0.0347	
DP				0.00122		0.00601		0.00335		0.00873

Table 5.3: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *chloroform* – 1,4 – *dioxane* system at 323.15 K.

$x_1$	$y_1(exp)$	$P(exp)$	$K=0.100$		$K=0.000$		$K=0.050$		$K=0.150$	
			$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$
0.0000	0.0000	0.15780	0.0000	0.16463	0.0000	0.16463	0.0000	0.16463	0.0000	0.16463
0.0932	0.1794	0.17503	0.2528	0.19947	0.2073	0.18780	0.2298	0.19341	0.2763	0.20598
0.1248	0.2383	0.18143	0.3227	0.21203	0.2715	0.19668	0.2969	0.20406	0.3486	0.22060
0.1757	0.3302	0.19296	0.4218	0.23304	0.3681	0.21218	0.3949	0.22223	0.4484	0.24465
0.2000	0.3691	0.19888	0.4639	0.24340	0.4113	0.22014	0.4376	0.23135	0.4899	0.25633
0.2626	0.4628	0.21367	0.5596	0.27101	0.5139	0.24236	0.5369	0.25621	0.5821	0.28682
0.3615	0.6184	0.24939	0.6798	0.31750	0.6510	0.28308	0.6655	0.29984	0.6941	0.33612
0.4750	0.7552	0.29810	0.7832	0.37497	0.7735	0.33885	0.7783	0.35662	0.7881	0.39387
0.5555	0.8378	0.34787	0.8396	0.41860	0.8400	0.38460	0.8398	0.40148	0.8394	0.43592
1.0000	1.0000	0.69336	0.9948	0.69336	0.9948	0.69336	0.9948	0.69336	0.9948	0.69336
$D_y$			0.0538		0.0251		0.0394		0.0681	
DP				0.04195		0.02151		0.03147		0.05297

Table 5.4: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *methanol* – 1,4 – *dioxane* system at 293.15 K.

$x_1$	$y_1(exp)$	$P(exp)$	$K=0.130$		$K=0.098$		$K=0.050$		$K=0.150$	
			$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$
0.0000	0.0000	0.03666	0.0000	0.03999	0.0000	0.03999	0.0000	0.0399	0.0000	0.03999
0.0091	0.0738	0.04002	0.0783	0.04301	0.0730	0.04276	0.0651	0.04240	0.0817	0.04317
0.0247	0.1762	0.04423	0.1863	0.04798	0.1750	0.04732	0.1581	0.04637	0.1933	0.04840
0.0418	0.2635	0.04994	0.2775	0.05315	0.2625	0.05207	0.2398	0.05051	0.2867	0.05384
0.0760	0.3888	0.05896	0.4070	0.06266	0.3891	0.06082	0.3615	0.05818	0.4180	0.06384
0.0961	0.4426	0.06333	0.4621	0.06778	0.4438	0.06554	0.4154	0.06234	0.4733	0.06921
0.1092	0.4722	0.06569	0.4924	0.07093	0.4741	0.06846	0.4456	0.06492	0.5035	0.07252
0.1586	0.5575	0.07262	0.5790	0.08166	0.5617	0.07842	0.5346	0.07378	0.5894	0.08375
0.1694	0.5721	0.07667	0.5936	0.08379	0.5767	0.08040	0.5501	0.07557	0.6038	0.08597
0.9870	0.9891	0.12886	0.9855	0.13566	0.9875	0.13539	0.9900	0.13503	0.9843	0.13584
$D_y$			0.0133		0.0017		0.0177		0.0208	
DP				0.00496		0.00342		0.00194		0.00595

Table 5.5: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *methanol* – *nitromethane* system at 303.15 K.

$x_1$	$y_1(exp)$	$P(exp)$	$K=0.150$		$K=0.110$		$K=0.000$		$K=0.050$	
			$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$
0.0000	0.0000	0.06344	0.0000	0.07581	0.0000	0.07581	0.0000	0.07581	0.0000	0.07581
0.1020	0.5400	0.13461	0.5649	0.15920	0.5411	0.15099	0.4690	0.13040	0.5030	0.13939
0.2090	0.6800	0.17726	0.6849	0.20391	0.6662	0.19229	0.6094	0.16328	0.6315	0.17726
0.4350	0.7450	0.20658	0.7538	0.23585	0.7464	0.22527	0.7252	0.19760	0.7349	0.20992
0.5260	0.7600	0.21191	0.7634	0.23938	0.7612	0.23029	0.7550	0.20576	0.7578	0.21682
0.6510	0.7900	0.21857	0.7753	0.24228	0.7808	0.23497	0.7954	0.21484	0.7889	0.22400
0.6770	0.8300	0.22124	0.7785	0.24282	0.7857	0.23581	0.8045	0.21652	0.7962	0.22529
0.8050	0.8400	0.22124	0.8088	0.24465	0.8227	0.23881	0.8577	0.22365	0.8424	0.23040
1.0000	1.0000	0.21351	1.0004	0.22763	1.0004	0.22763	1.0004	0.22763	1.0004	0.22763
$D_y$			0.0155		0.0098		0.0239		0.0151	
DP				0.02257		0.01594		0.00785		0.00646

Table 5.6: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *tetrachloromethane* – *ethanol* system at 323.15 K.

$x_1$	$y_1(exp)$	$P(exp)$	$K=0.000$		$K=0.150$	
			$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$
0.1000	0.3370	0.405304	0.2835	0.378224	0.3931	0.448225
0.2000	0.4980	0.486605	0.4311	0.435247	0.5213	0.528337
0.3000	0.5810	0.536452	0.5212	0.474096	0.5775	0.566931
0.4000	0.6230	0.561375	0.5818	0.499128	0.6045	0.583188
0.5000	0.6420	0.570838	0.6256	0.513929	0.6180	0.588892
0.6000	0.6470	0.572171	0.6598	0.521336	0.6260	0.590395
0.7000	0.6460	0.572971	0.6903	0.523256	0.6350	0.589859
0.8000	0.6530	0.569372	0.7259	0.519229	0.6551	0.583948
0.9000	0.7050	0.542316	0.7906	0.500964	0.7168	0.554971
1.0000	1.0000	0.414501	1.0005	0.426474	1.0005	0.426474
$D_y$			0.0454		0.0172	
$DP$				0.046397		0.022931

Table 5.7: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *tetrachloromethane* – 1,4 – *dioxane* system at 298.15 K.

$x_1$	$y_1(exp)$	$P(exp)$	$K=0.000$		$K=0.010$	
			$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$
0.0000	0.0000	0.048914	0.0000	0.051812	0.0000	0.051812
0.0747	0.2193	0.058510	0.2359	0.062814	0.2916	0.067828
0.2004	0.4654	0.074370	0.4797	0.080202	0.5340	0.090461
0.2995	0.5933	0.086232	0.6025	0.092864	0.6388	0.104817
0.3710	0.6632	0.095162	0.6697	0.101423	0.6924	0.113551
0.4717	0.7406	0.105958	0.7448	0.112662	0.7506	0.123964
0.5708	0.8007	0.112622	0.8040	0.122829	0.7970	0.132544
0.6554	0.8440	0.119685	0.8470	0.130910	0.8325	0.138971
0.7588	0.8913	0.128082	0.8940	0.140162	0.8751	0.146064
1.0000	1.0000	0.151273	1.0005	0.160316	1.0005	0.160316
$D_y$			0.0060		0.0257	
$DP$				0.007519		0.014952

Table 5.8: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *tetrachloromethane* – 1 – *propanol* system at 298.15 K.

$x_1$	$y_1(exp)$	$P(exp)$	$K=0.150$		$K=0.070$	
			$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$
0.0825	0.3850	0.49167	0.4424	0.53683	0.3822	0.48505
0.1260	0.4760	0.55611	0.5380	0.62281	0.4780	0.55611
0.2125	0.5920	0.67413	0.6421	0.74944	0.5965	0.66307
0.2775	0.6460	0.73543	0.6850	0.81293	0.6498	0.72422
0.4600	0.7350	0.84446	0.7412	0.89983	0.7332	0.82855
0.5700	0.7730	0.88624	0.7558	0.91829	0.7623	0.86061
0.6320	0.7880	0.90203	0.7625	0.92422	0.7762	0.87263
0.8080	0.8260	0.91936	0.7938	0.93157	0.8220	0.89102
0.8775	0.8470	0.91503	0.8249	0.92434	0.8539	0.88934
0.9120	0.8700	0.91136	0.8532	0.91136	0.8777	0.88388
$D_y$			0.0328		0.0056	
$DP$				0.03958		0.01813

Table 5.9: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *chloroform* – *ethanol* system at 328.15 K.

$x_1$	$y_1(exp)$	$P(exp)$	$K=0.150$		$K=0.070$	
			$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$
0.0210	0.0750	0.394509	0.1098	0.415073	0.0860	0.404282
0.1060	0.3210	0.491137	0.3849	0.552166	0.3302	0.506706
0.1600	0.4280	0.550047	0.4852	0.625383	0.4320	0.565276
0.2110	0.5130	0.606024	0.5527	0.684954	0.5057	0.615834
0.2590	0.5720	0.653072	0.6006	0.732841	0.5661	0.653072
0.3030	0.6160	0.692923	0.6351	0.770283	0.6047	0.692923
0.3430	0.6470	0.721311	0.6609	0.799261	0.6381	0.721311
0.3850	0.6700	0.749300	0.6834	0.825114	0.6674	0.749300
$D_y$			0.0338		0.0075	
$DP$				0.068344		0.006298

Table 5.10: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *chloroform – methanol* system at 308.15 K.

$x_1$	$y_1(exp)$	$P(exp)$	$K=0.150$		$K=0.1000$	
			$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$
0.1000	0.2630	0.337598	0.3123	0.384619	0.2797	0.366746
0.2000	0.4310	0.393976	0.4521	0.443325	0.4236	0.418544
0.3000	0.5390	0.438358	0.5284	0.478097	0.5107	0.452651
0.4000	0.6100	0.467280	0.5756	0.497520	0.5692	0.474034
0.5000	0.6540	0.483140	0.6084	0.507533	0.6162	0.483140
0.6000	0.6840	0.488738	0.6346	0.511682	0.6513	0.488738
0.7000	0.7040	0.491670	0.6601	0.511488	0.6804	0.491670
0.8000	0.7240	0.488471	0.6938	0.505380	0.7154	0.488471
0.9000	0.7760	0.473411	0.7611	0.483181	0.7762	0.473411
0.9500	0.8450	0.453152	0.8381	0.453152	0.8520	0.445605
$D_y$			0.0306		0.0203	
DP				0.026018		0.008231

Table 5.11: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for 1,2 – *dichloroethane – 1 – propanol* system at 353.15 K.

$x_1$	$y_1(exp)$	$P(exp)$	$K=0.150$		$K=0.140$	
			$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$
0.1000	0.3060	0.639744	0.3195	0.674373	0.3132	0.668179
0.2000	0.4730	0.749034	0.4733	0.795006	0.4671	0.785520
0.3000	0.5870	0.836998	0.5599	0.874997	0.5554	0.864515
0.4000	0.6640	0.888978	0.6138	0.923860	0.6113	0.913809
0.5000	0.7030	0.926296	0.6502	0.951757	0.6498	0.942697
0.6000	0.7340	0.948954	0.6785	0.966331	0.6866	0.948954
0.7000	0.7730	0.958283	0.7066	0.971761	0.7141	0.958283
0.8000	0.7970	0.962282	0.7477	0.962282	0.7469	0.962282
0.9000	0.8600	0.955884	0.8148	0.936071	0.8191	0.930824
$D_y$			0.0400		0.0386	
DP				0.025512		0.017637

Table 5.12: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *diisopropylether* – *benzene* system at 323.15 K.

$x_1$	$y_1(exp)$	$P(exp)$	$K=0.100$		$K=0.000$	
			$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$
0.0370	0.0660	0.375850	0.0921	0.375850	0.0651	0.366148
0.1560	0.2410	0.415967	0.2943	0.432175	0.2417	0.398236
0.3340	0.4400	0.456884	0.4751	0.484467	0.4470	0.438943
0.4670	0.5660	0.477542	0.5754	0.509860	0.5743	0.465265
0.5840	0.6720	0.492603	0.6576	0.526274	0.6757	0.486324
0.7110	0.7700	0.511795	0.7494	0.539320	0.7723	0.511795
0.8100	0.8500	0.526856	0.8271	0.546200	0.8498	0.526856
0.8800	0.9060	0.535919	0.8867	0.549238	0.9055	0.535919
$D_y$			0.0252		0.0030	
$DP$				0.021246		0.007991

Table 5.13: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *diisopropylether* – *toluene* system at 343.15 K.

$x_1$	$y_1(exp)$	$P(exp)$	$K=0.000$		$K=0.1000$	
			$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$
0.0440	0.1630	0.312408	0.1766	0.312408	0.2264	0.335283
0.0600	0.2130	0.327336	0.2286	0.327336	0.2858	0.357476
0.0860	0.2810	0.353059	0.3013	0.353059	0.3656	0.392167
0.1860	0.4780	0.444089	0.5027	0.444089	0.5603	0.510615
0.2660	0.5770	0.509929	0.6055	0.516198	0.6510	0.590562
0.2700	0.5850	0.511928	0.6100	0.519550	0.6548	0.594224
0.2900	0.6070	0.530854	0.6314	0.536427	0.6722	0.612454
0.3780	0.6920	0.601626	0.7112	0.608497	0.7351	0.685587
0.8000	0.9330	0.927496	0.9349	0.927496	0.9181	0.959162
0.8880	0.9620	1.003598	0.9571	1.003598	0.9611	1.003598
$D_y$			0.0178		0.0571	
$DP$				0.002634		0.051880



Table 5.14: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for 1,4 - *dioxane* - *toluene* system at 353.15 K.

$x_1$	$y_1(exp)$	$P(exp)$	$K=0.000$		$K=0.100$	
			$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$
0.0000	0.0000	0.390510	0.0000	0.390510	0.0000	0.390510
0.1250	0.1680	0.416233	0.1754	0.416233	0.2167	0.435005
0.2500	0.3180	0.439158	0.3221	0.439158	0.3684	0.471551
0.3750	0.4410	0.462082	0.4540	0.454655	0.4831	0.498185
0.5000	0.5630	0.479275	0.5705	0.471392	0.5776	0.516478
0.6250	0.6750	0.491004	0.6795	0.485696	0.6643	0.527754
0.7500	0.7850	0.498334	0.7841	0.498334	0.7544	0.532378
0.8750	0.8880	0.505398	0.8946	0.505398	0.8605	0.529253
1.0000	1.0000	0.509663	1.0002	0.515295	1.0002	0.515295
$D_y$			0.0049		0.0250	
DP				0.002917		0.024973

Table 5.15: Comparison of experimental and calculated values of  $y_i$  and  $p$  from Wong-Sandler mixing rules for *ethanol* - 1 - *propanol* system at 283.15K.

$x_1$	$y_1(exp)$	$P(exp)$	$K=0.000$	
			$y_1(cal)$	$P(cal)$
0.0000	0.0000	0.009863	0.0000	0.008872
0.1000	0.4800	0.016393	0.4763	0.015272
0.2000	0.6600	0.023191	0.6685	0.021498
0.3000	0.7700	0.029055	0.7753	0.027775
0.4000	0.8300	0.035586	0.8443	0.034239
0.5000	0.8800	0.042116	0.8925	0.040956
0.6000	0.9200	0.048381	0.9193	0.048381
0.7000	0.9400	0.054911	0.9585	0.054911
0.8000	0.9600	0.059709	0.9741	0.062540
1.0000	1.0000	0.073571	1.0001	0.077146
$D_y$			0.0078	
DP				0.001400

Table 5.16: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *ethanol – toluene* system at 308.15 K.

$x_1$	$y_1(exp)$	$P(exp)$	$K=0.150$		$K=0.1200$	
			$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$
0.1380	0.5910	0.265894	0.5842	0.265894	0.5681	0.255183
0.3340	0.6590	0.313208	0.6883	0.321753	0.6773	0.309586
0.4370	0.6810	0.321205	0.7054	0.330151	0.6940	0.321205
0.5330	0.7050	0.326536	0.7155	0.333910	0.7080	0.326536
0.6340	0.7130	0.329202	0.7262	0.336326	0.7261	0.329202
0.7360	0.7390	0.331867	0.7445	0.337751	0.7491	0.331867
0.8060	0.7660	0.328535	0.7683	0.336925	0.7830	0.328535
0.8850	0.8390	0.321871	0.8182	0.331043	0.8396	0.321871
0.9460	0.9020	0.311209	0.8892	0.318844	0.9001	0.314822
$D_y$			0.0140		0.0111	
$DP$				0.007008		0.001994

Table 5.17: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for 1 – *hexene* – 1,4 – *dioxane* system at 353.15 K.

$x_1$	$y_1(exp)$	$P(exp)$	$K=0.100$		$K=0.030$	
			$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$
0.0150	0.0950	0.554578	0.1195	0.577369	0.0963	0.562607
0.0580	0.2770	0.672264	0.3317	0.731881	0.2834	0.683211
0.1080	0.4150	0.802612	0.4649	0.875853	0.4126	0.802612
0.2850	0.6290	1.092763	0.6566	1.187916	0.6231	1.092763
0.4890	0.7450	1.322271	0.7464	1.373835	0.7431	1.291227
0.7420	0.8550	1.352792	0.8503	1.524093	0.8640	1.477351
0.8850	0.9300	1.459149	0.9254	1.602537	0.9368	1.578068
$D_y$			0.0239		0.0048	
$DP$				0.088151		0.041928

Table 5.18: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *methanol – acetonitrile* system at 303.15 K.

$x_1$	$y_1(exp)$	$P(exp)$	$K=0.150$		$K=0.070$	
			$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$
0.1500	0.3400	0.195922	0.3768	0.219124	0.3354	0.205264
0.2600	0.4510	0.215914	0.4852	0.242897	0.4469	0.224656
0.2870	0.4600	0.220712	0.5039	0.246985	0.4676	0.228170
0.4000	0.5090	0.233240	0.5642	0.258950	0.5395	0.239191
0.6180	0.6400	0.242969	0.6447	0.267731	0.6523	0.249291
0.6370	0.6520	0.245235	0.6516	0.267915	0.6623	0.249639
0.8000	0.7700	0.239637	0.7306	0.264230	0.7646	0.248202
0.8800	0.8390	0.231907	0.7983	0.256400	0.8354	0.243521
$D_y$			0.0256		0.0098	
DP				0.023511		0.007800

Table 5.19: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *methanol – 1, 2 – dichloroethane* system at 313.15 K.

$x_1$	$y_1(exp)$	$P(exp)$	$K=0.150$		$K=0.1000$	
			$y_1(cal)$	$P(cal)$	$y_1(cal)$	$P(cal)$
0.0000	0.0000	0.19992	0.0000	0.18452	0.0000	0.18452
0.1000	0.4790	0.353725	0.4968	0.339103	0.4791	0.327657
0.2000	0.5690	0.404505	0.5964	0.399854	0.5808	0.384813
0.3000	0.5920	0.426363	0.6314	0.426363	0.6216	0.409174
0.4000	0.6030	0.433160	0.6540	0.433160	0.6434	0.420341
0.5000	0.6050	0.435559	0.6678	0.435559	0.6589	0.426187
0.6000	0.6140	0.437025	0.6796	0.437025	0.6749	0.429734
0.7000	0.6400	0.436359	0.6902	0.442134	0.6980	0.431213
0.8000	0.6970	0.427029	0.7255	0.438369	0.7402	0.427029
0.9000	0.8100	0.402106	0.8041	0.420670	0.8190	0.412378
$D_y$			0.0348		0.0307	
DP				0.007035		0.012325

Table 5.20: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *methanol* – 1 – *propanol* system at 283.15 K.

$x_1$	$y_1(exp)$	$P(exp)$	$K=0.000$	
			$y_1(cal)$	$P(cal)$
0.0000	0.0000	0.009863	0.0000	0.008872
0.1000	0.4800	0.016393	0.4763	0.015272
0.2000	0.6600	0.023191	0.6685	0.021498
0.3000	0.7700	0.029055	0.7753	0.027775
0.4000	0.8300	0.035586	0.8443	0.034239
0.5000	0.8800	0.042116	0.8925	0.040956
0.6000	0.9200	0.048381	0.9193	0.048381
0.7000	0.9400	0.054911	0.9585	0.054911
0.8000	0.9600	0.059709	0.9741	0.062540
1.0000	1.0000	0.073571	1.0001	0.077146
$D_y$			0.0078	
$DP$				0.001400

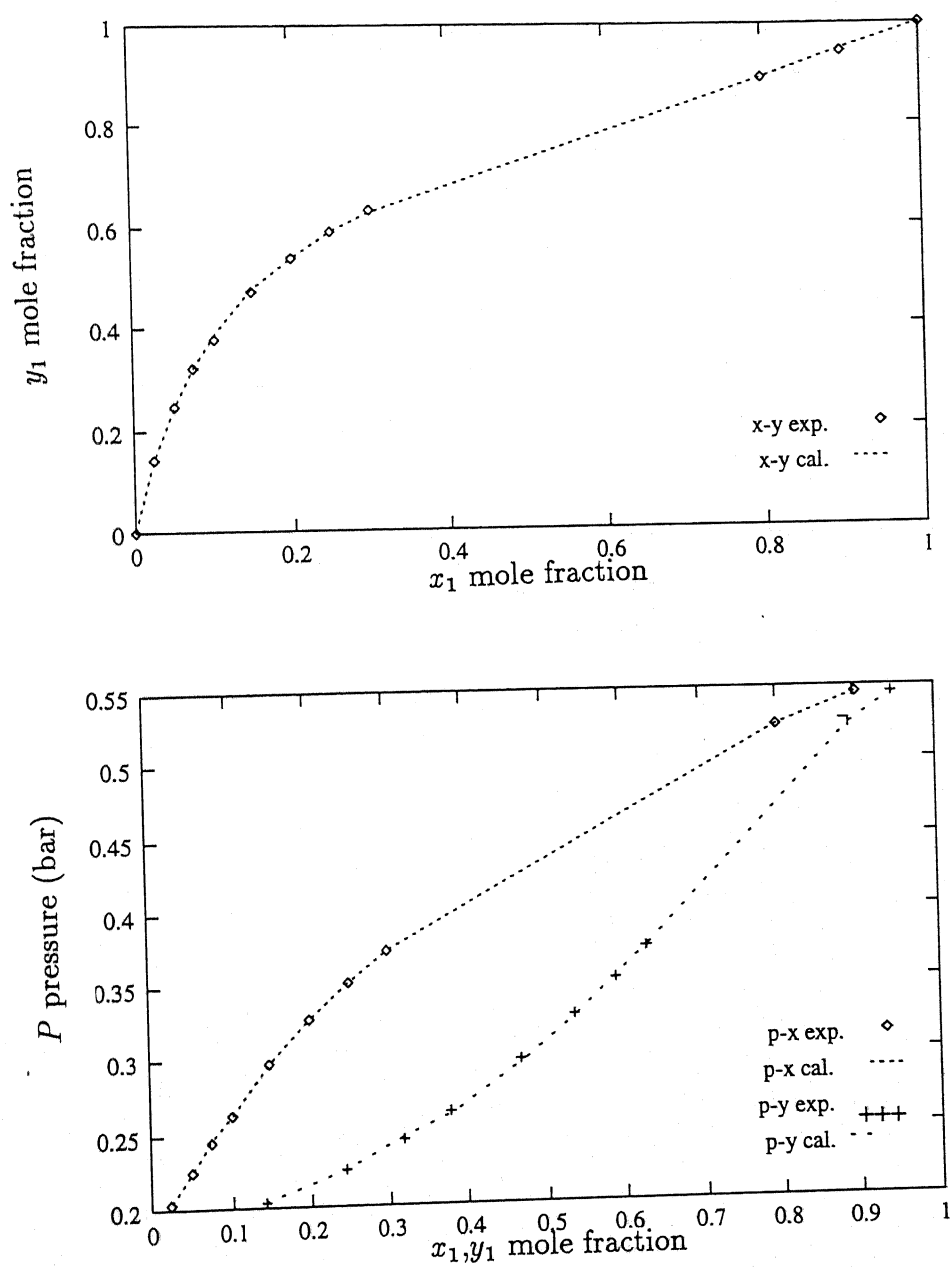


Figure 5.1: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for acetone – ethanol system at 313.15 k.

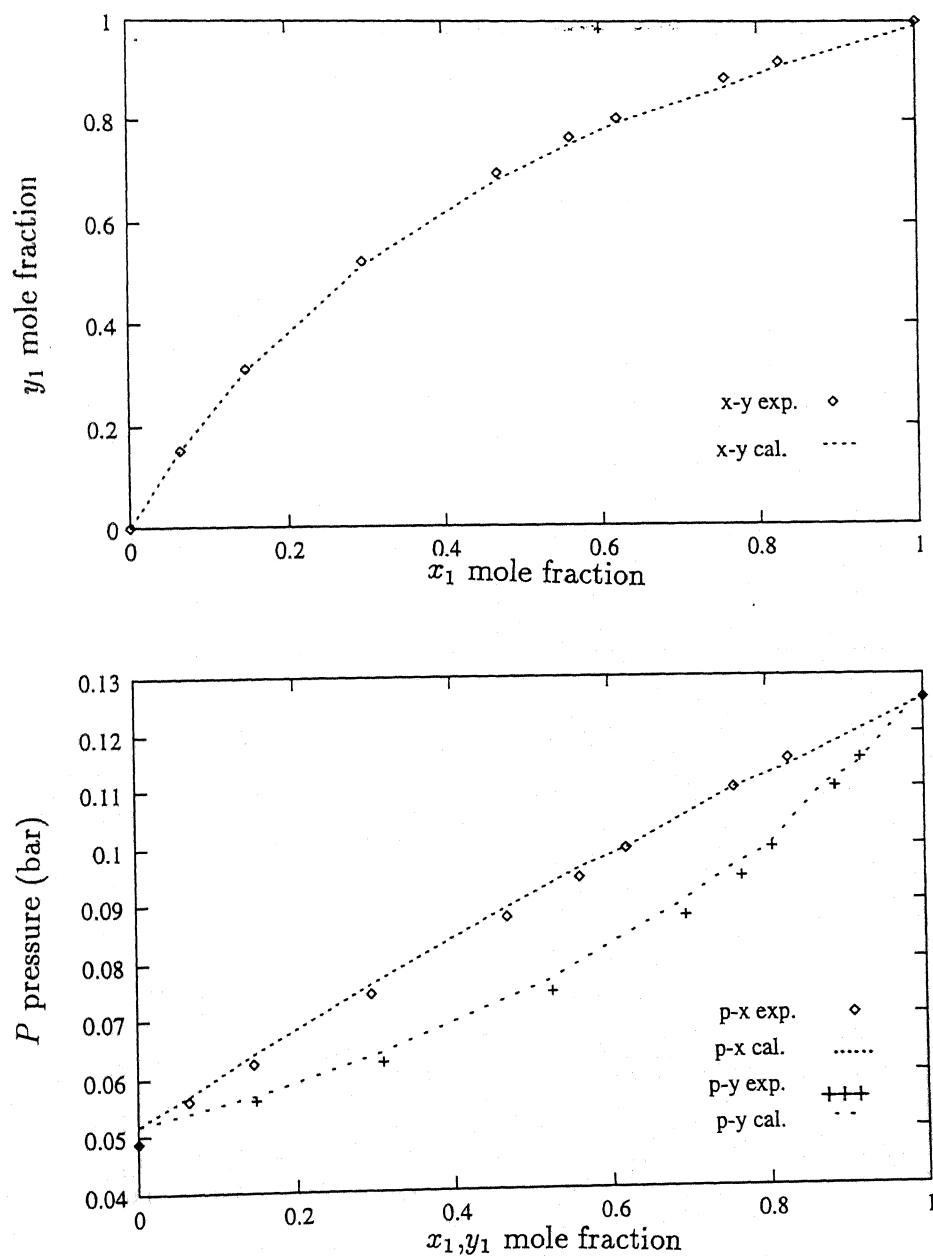


Figure 5.2: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *benzene* – 1,4 – *dioxane* system at 298.15 K.

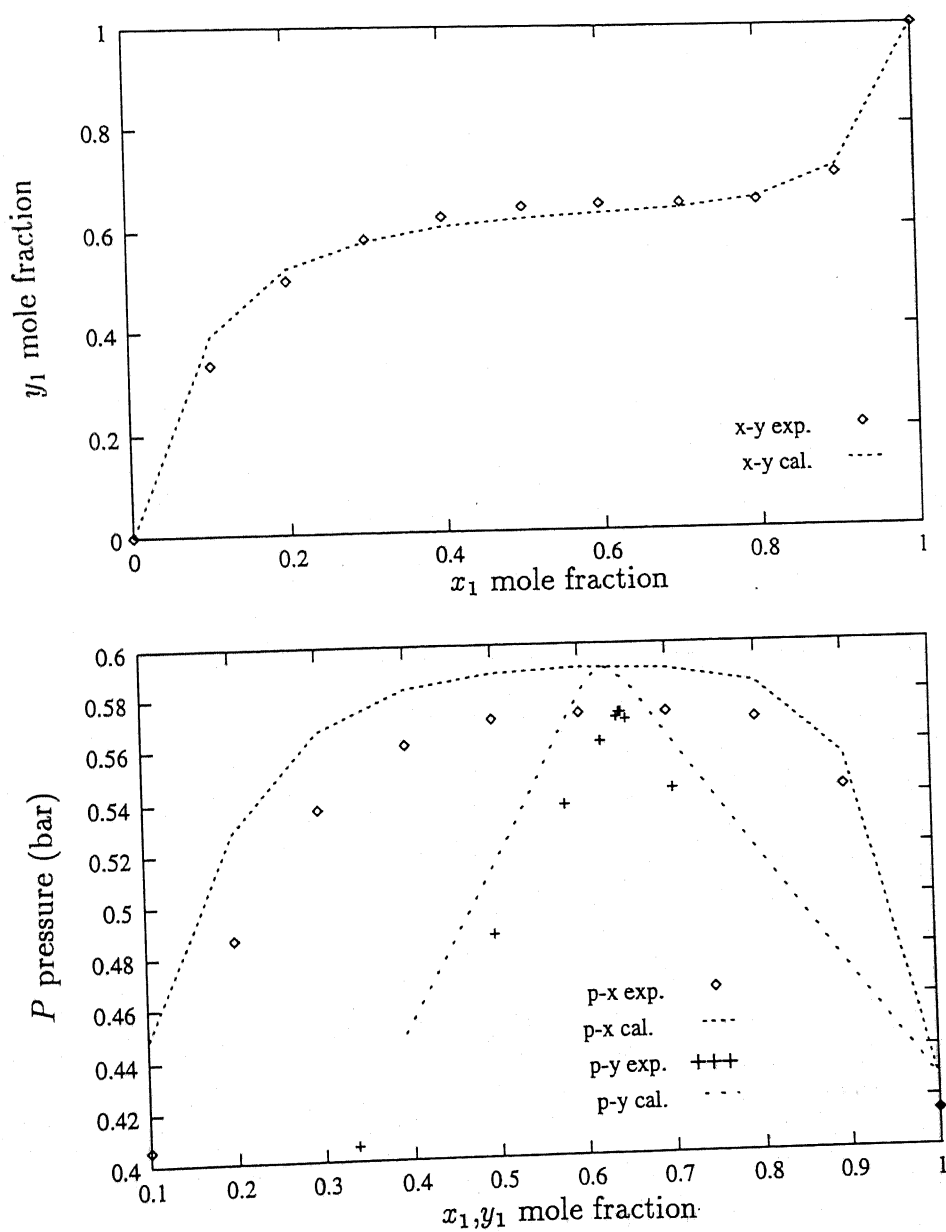


Figure 5.3: Comparison of experimental and calculated values of  $y_1$  and  $P$  from Wong-Sandler mixing rules for *tetrachloromethane* – *ethanol* system at 323.15 K.

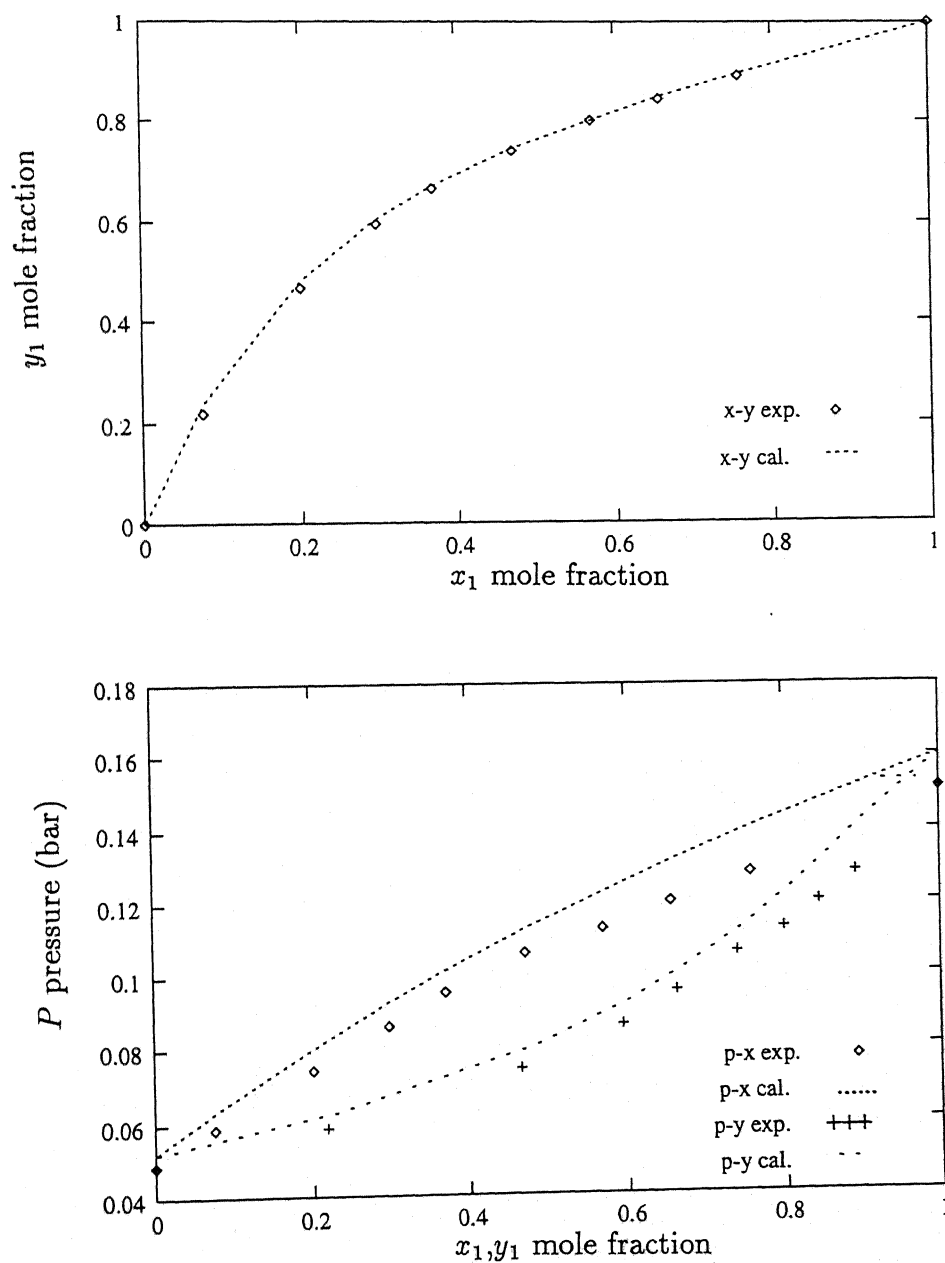


Figure 5.4: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *tetrachloromethane* – *1,4-dioxane* system at 298.15 K.



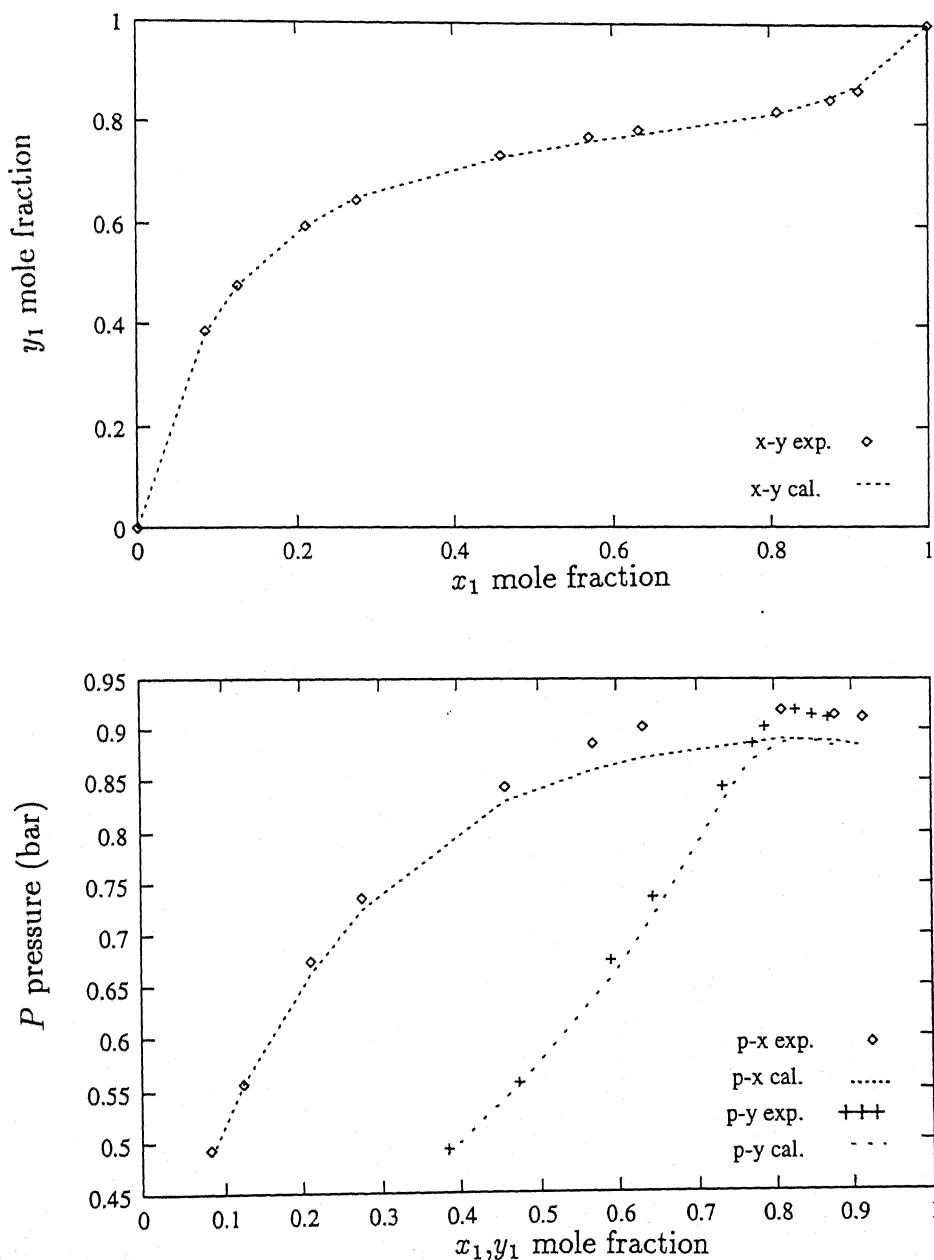


Figure 5.5: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *tetrachloromethane* – 1 – *propanol* system at 343.15 K.

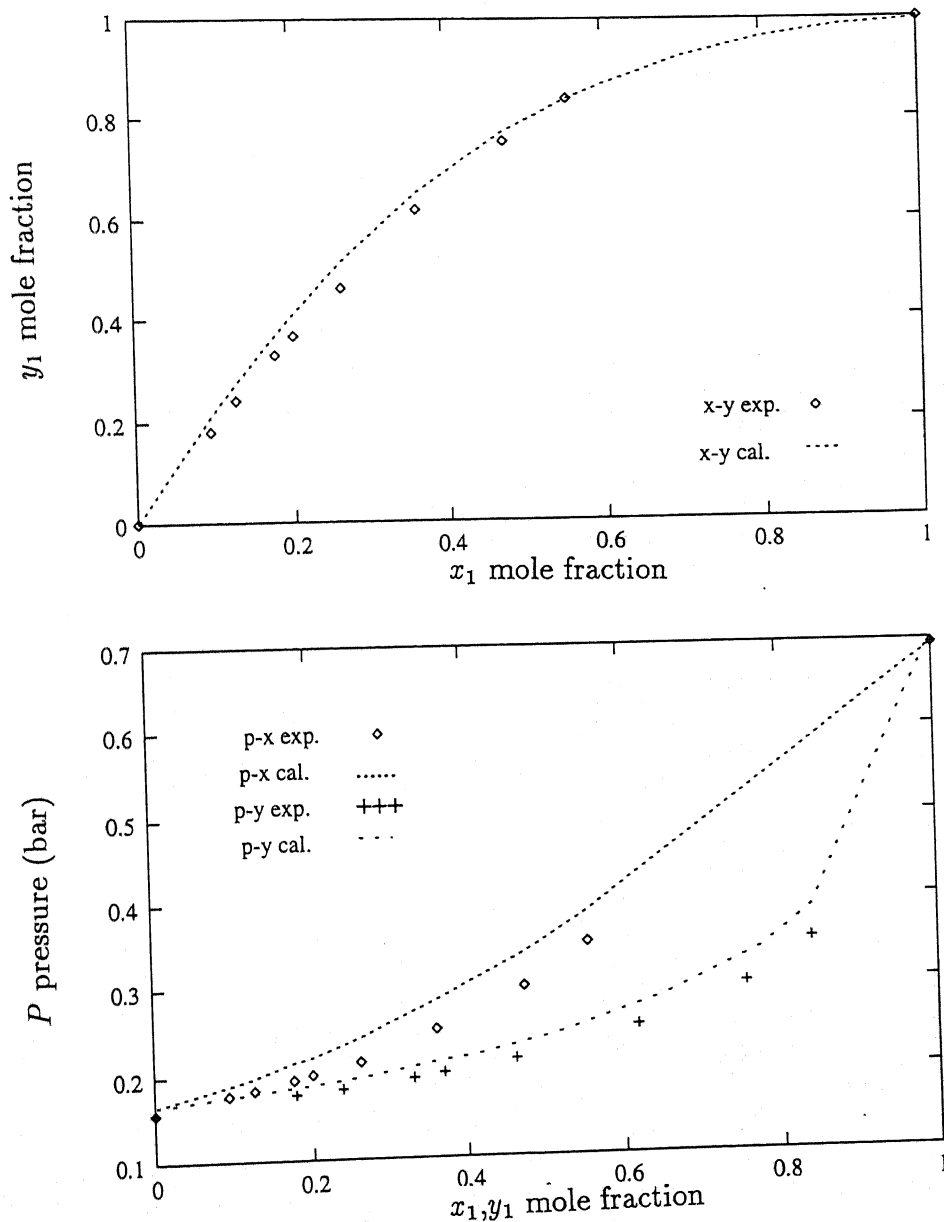


Figure 5.6: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *chloroform* – 1,4 – *dioxane* system at 323.15 K.

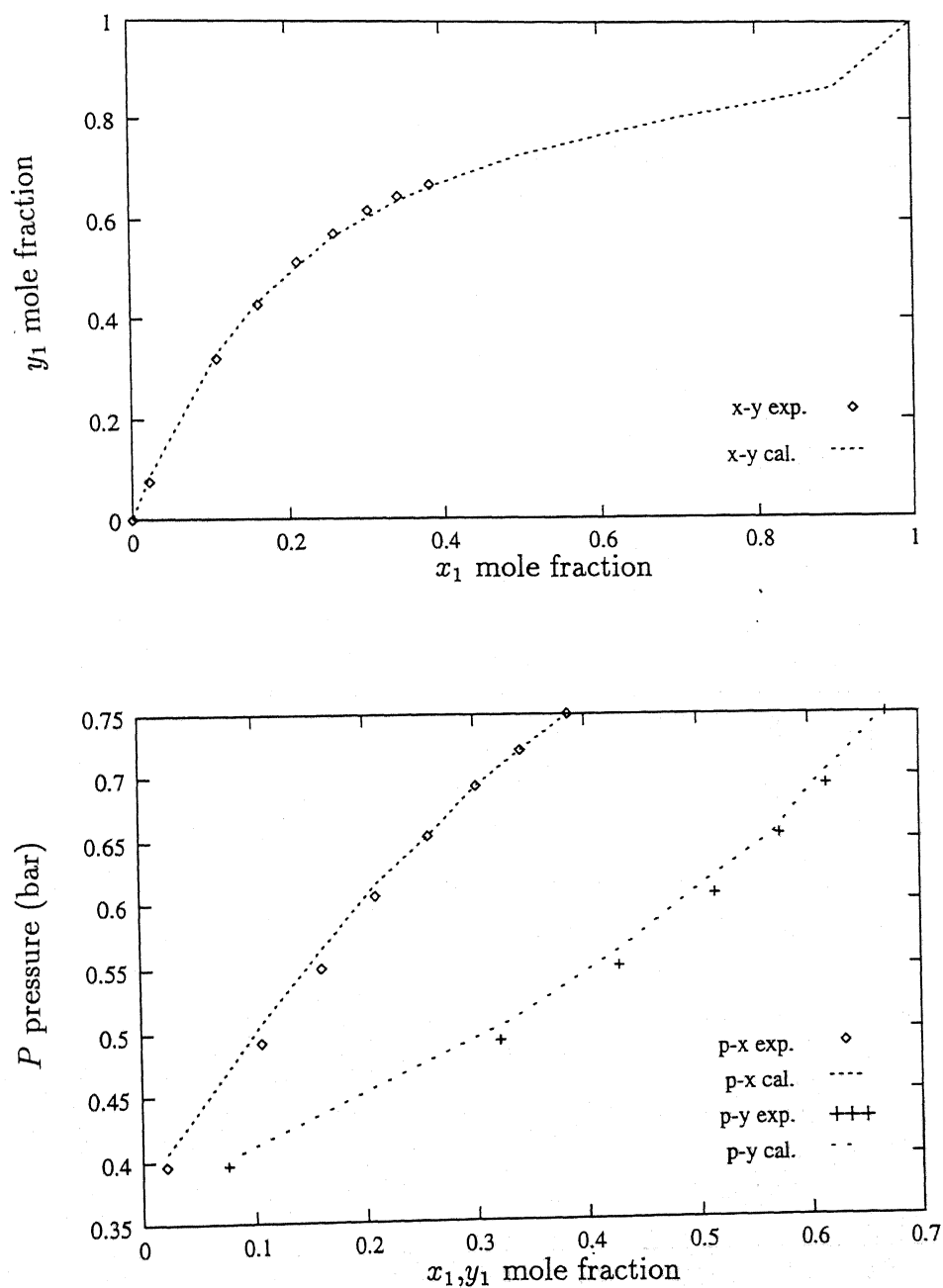


Figure 5.7: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *chloroform* – *ethanol* system at 328.15 K.

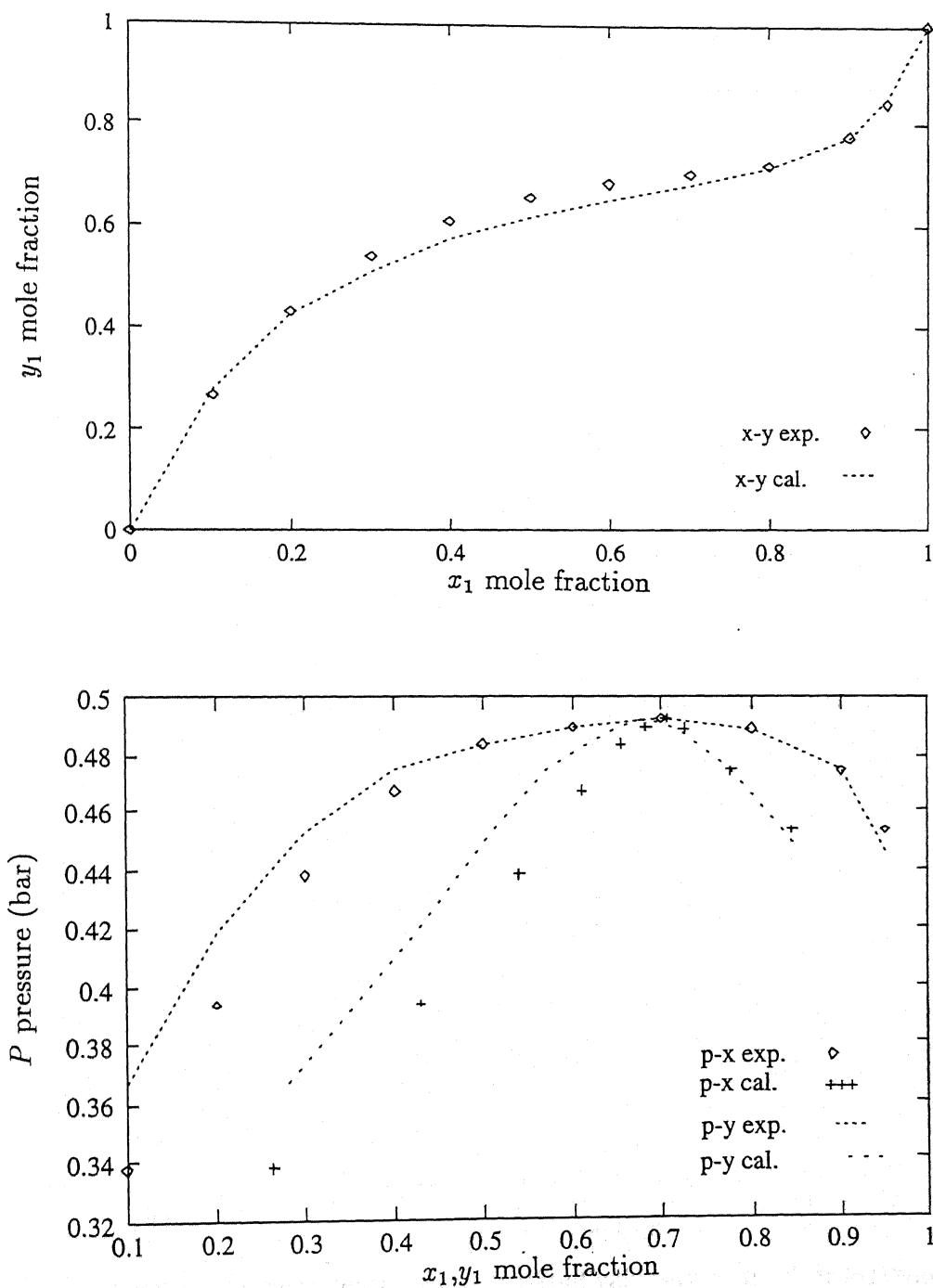


Figure 5.8: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *chloroform* – *methanol* system at 308.15 K.

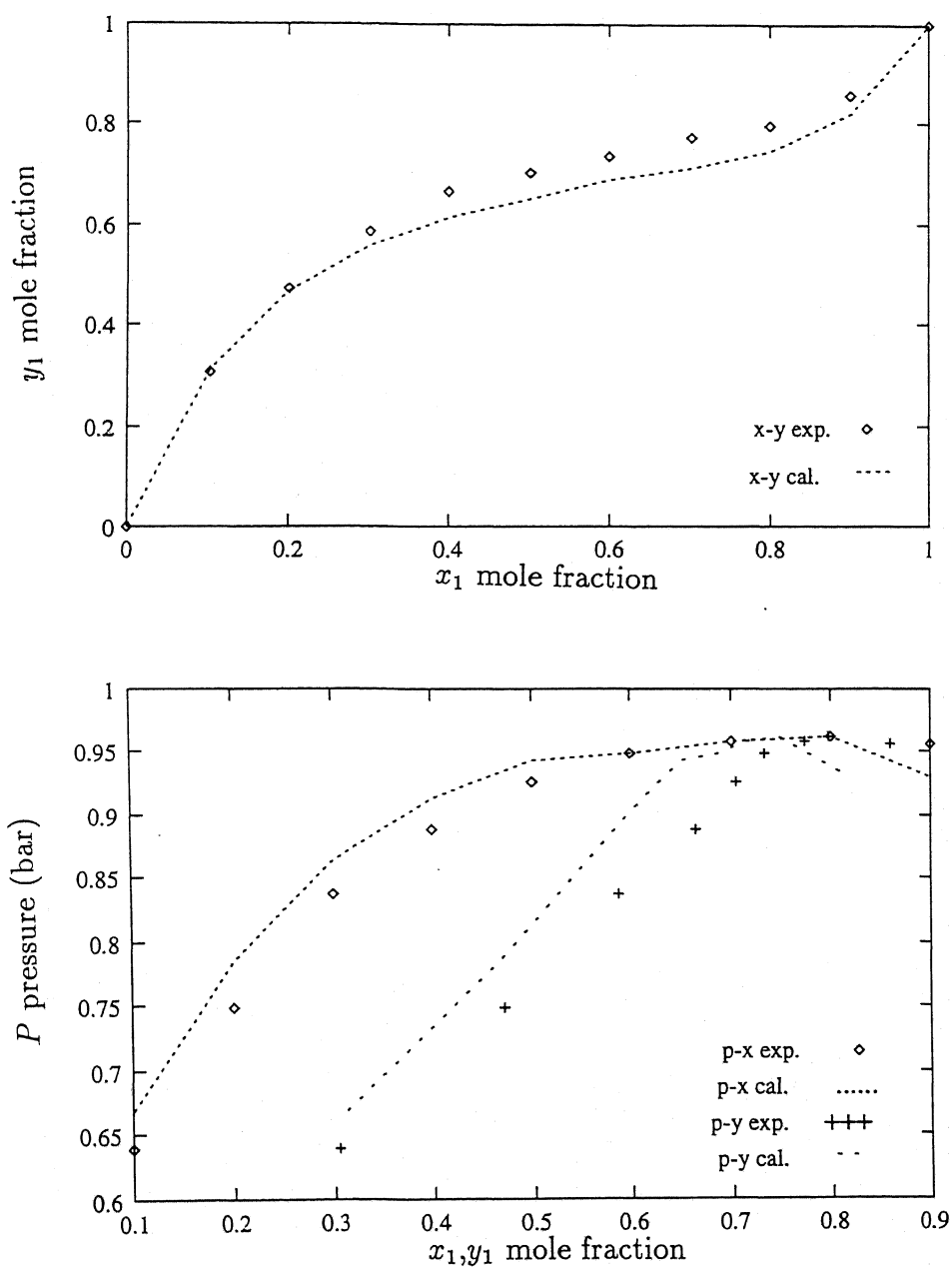


Figure 5.9: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for 1,2 - *dichloroethane* - 1 - *propanol* system at 353.15 K.

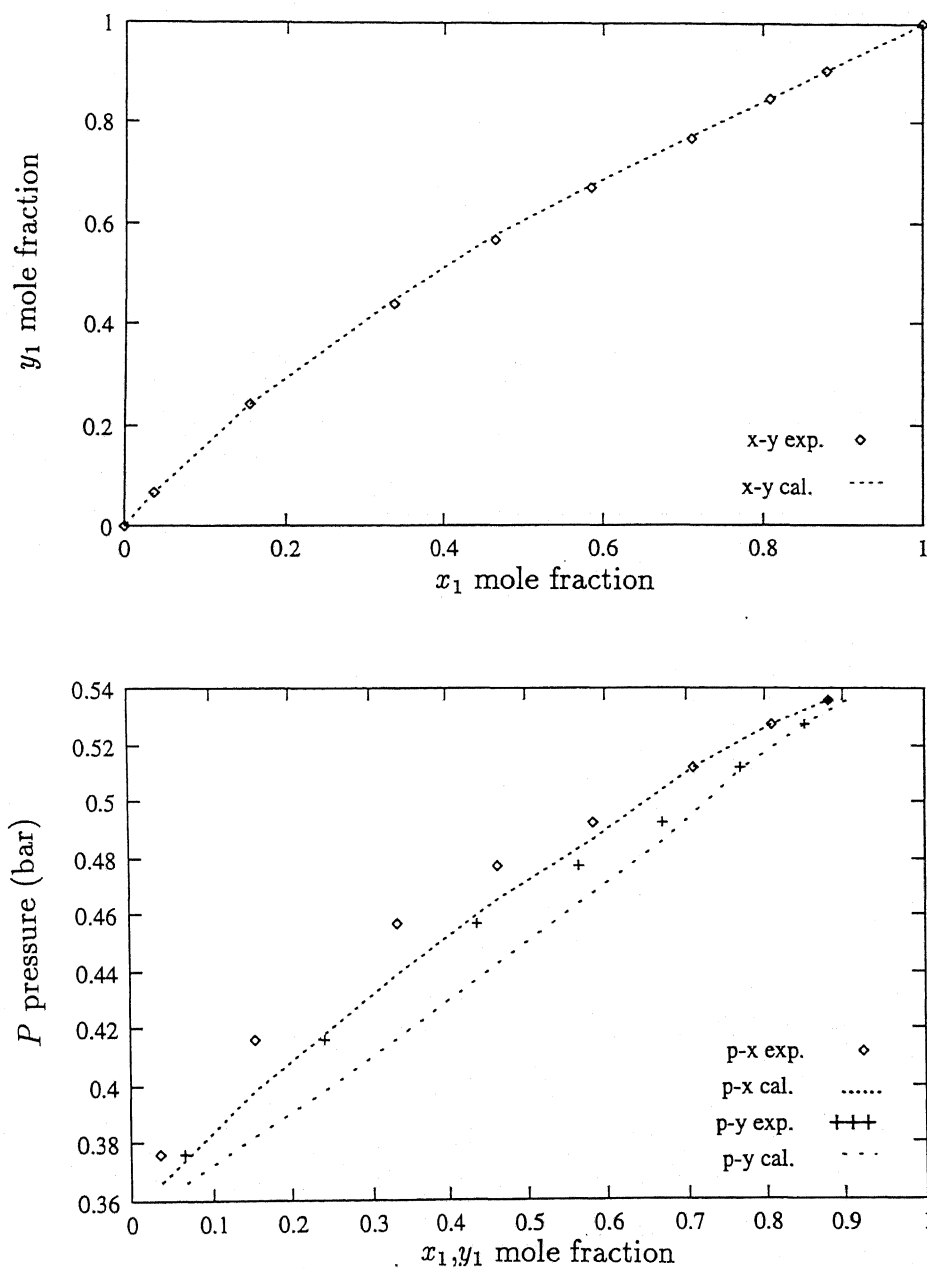


Figure 5.10: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *diisopropylether* – *benzene* system at 323.15 K.

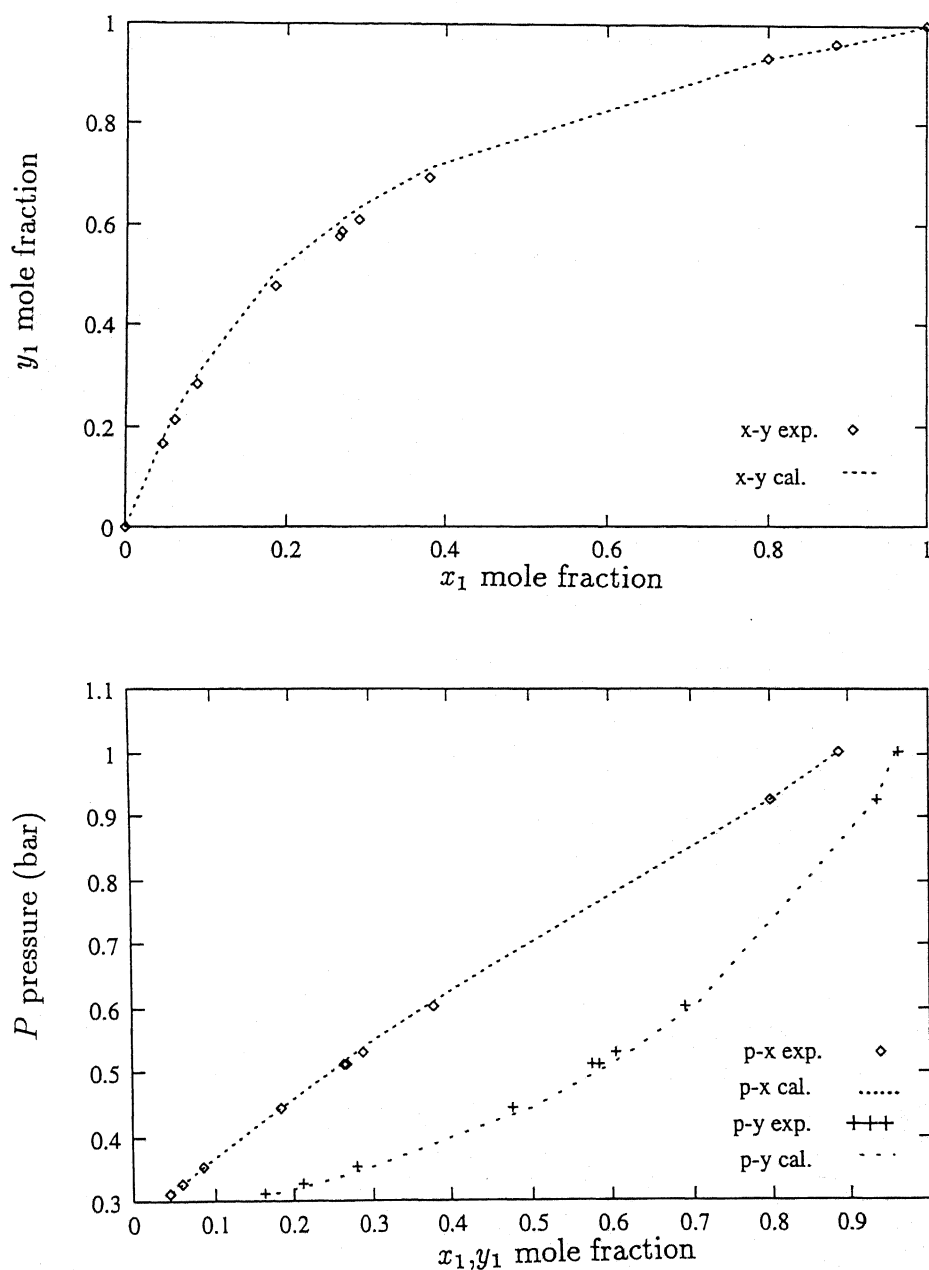


Figure 5.11: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for diisopropylether - toluene system at 353.15 K.

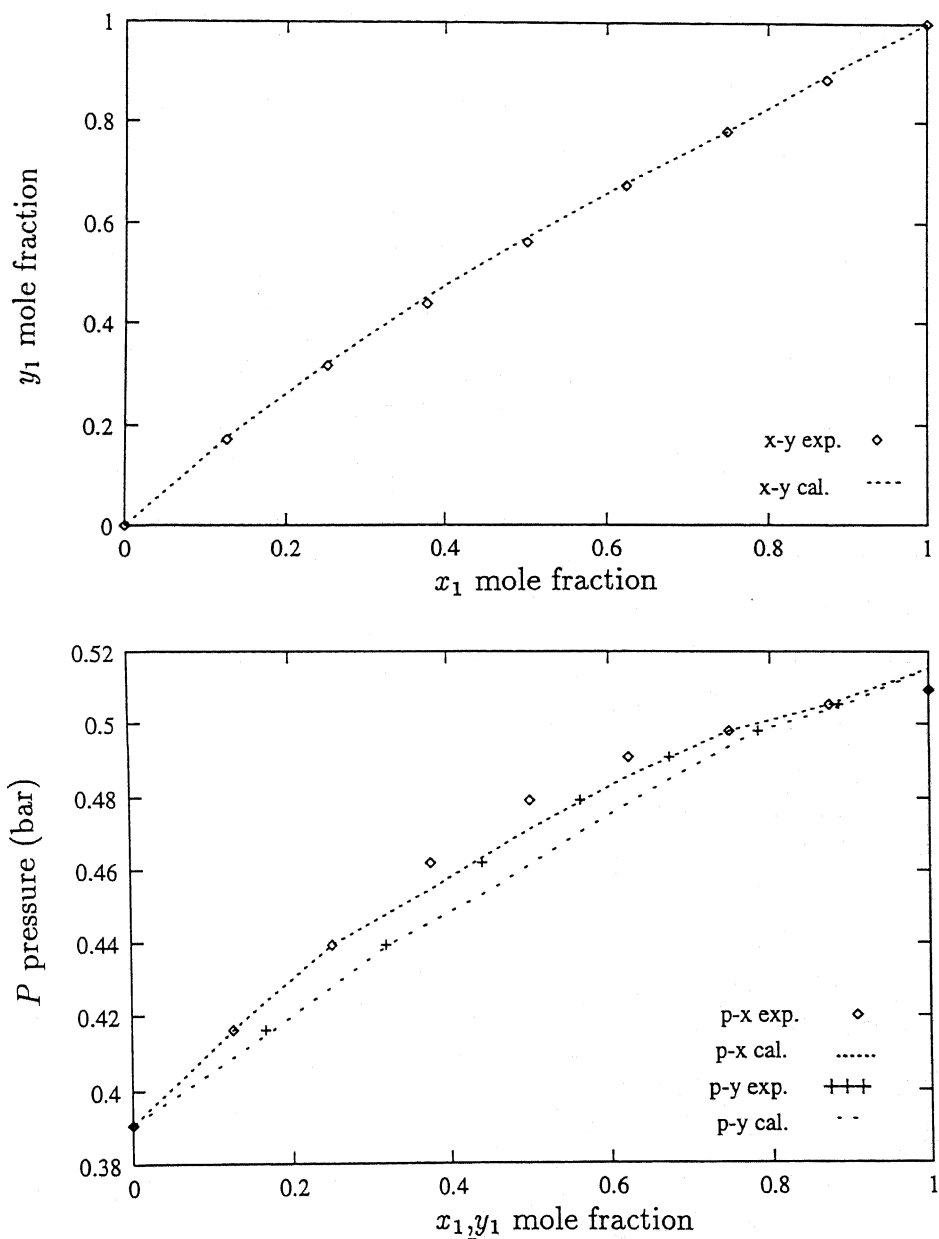


Figure 5.12: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for 1,4 - dioxane - toluene system at 353.15 K.



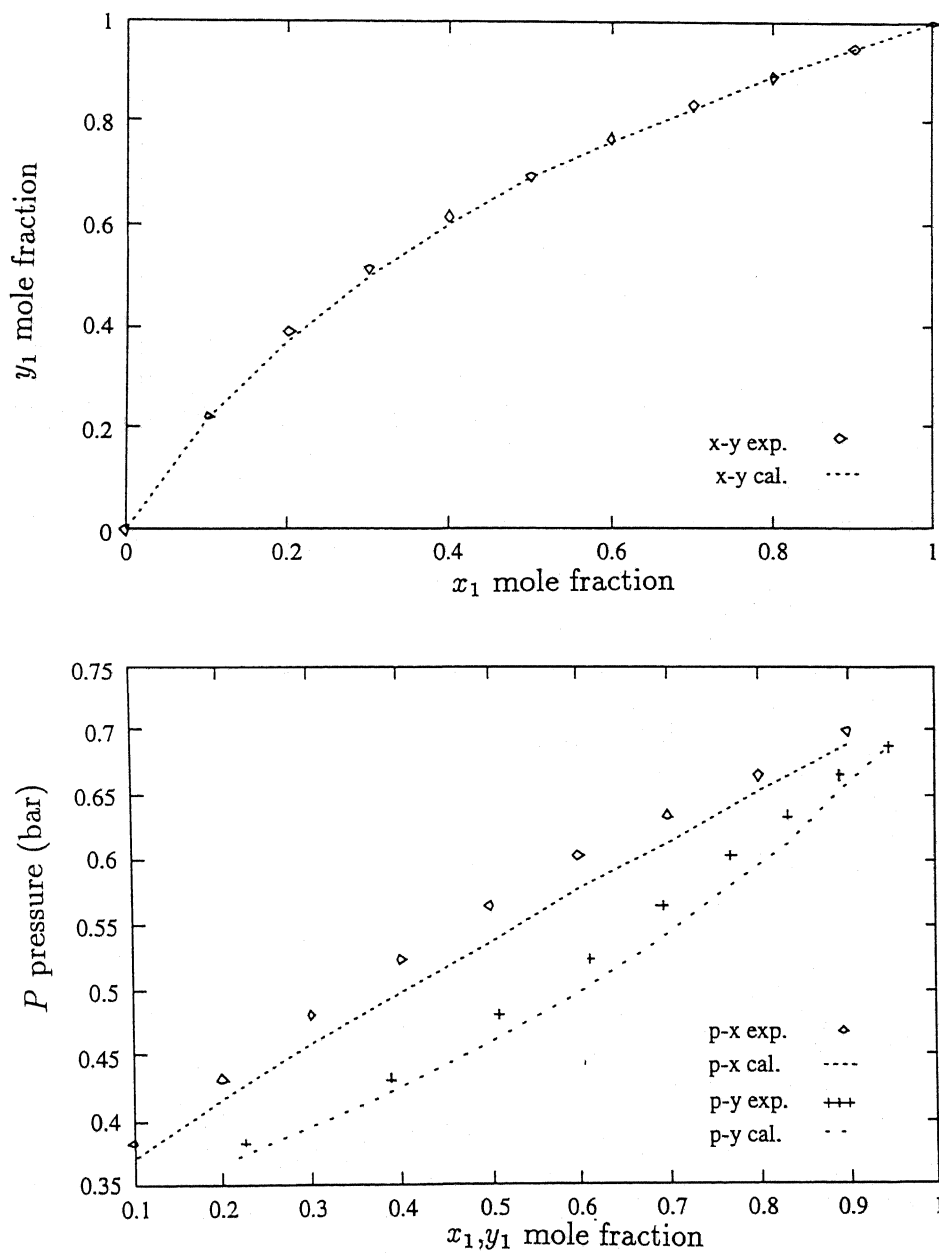


Figure 5.13: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *ethanol* – 1 – *propanol* system at 343.15 K.

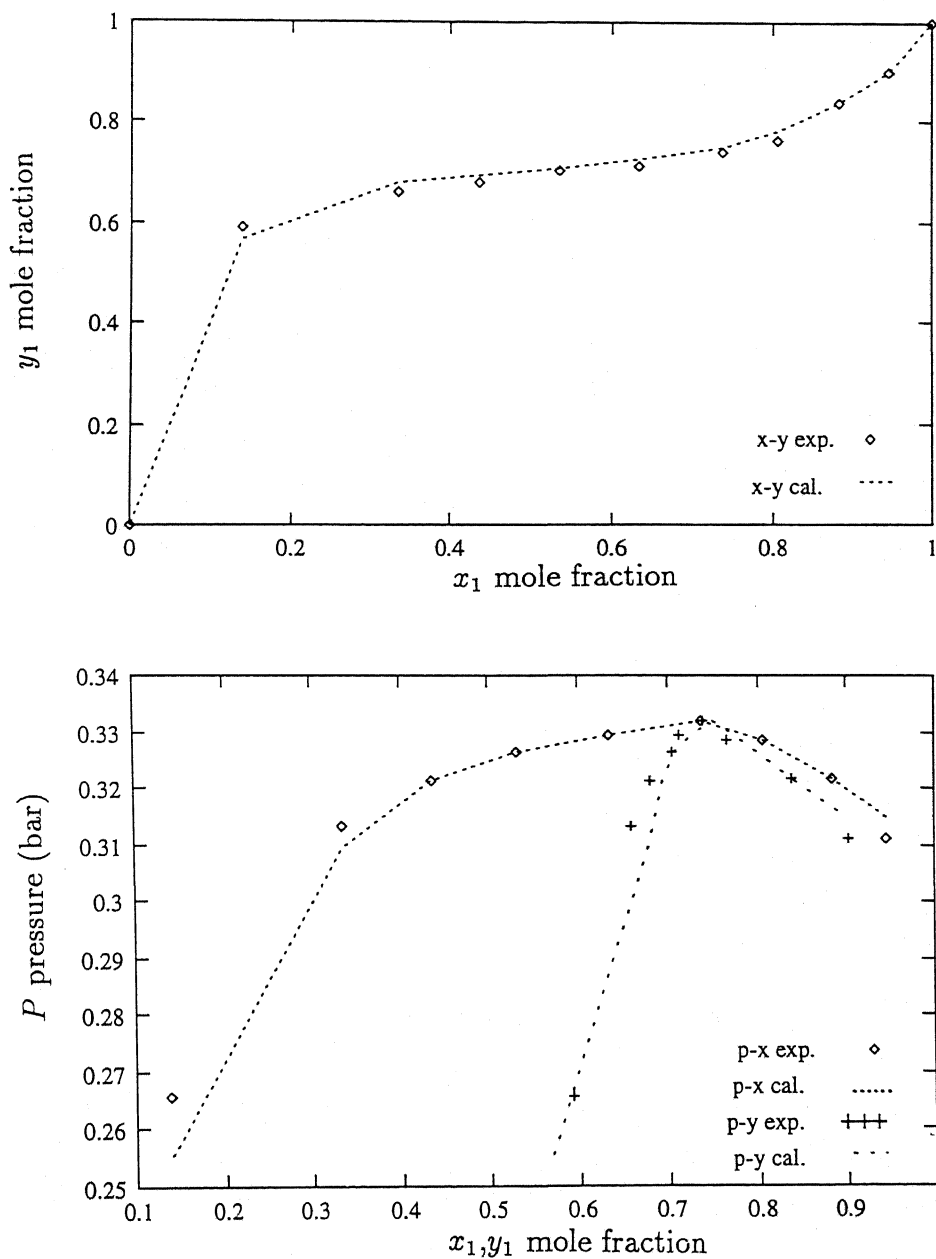


Figure 5.14: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *ethanol* – *toluene* system at 323.15 K.

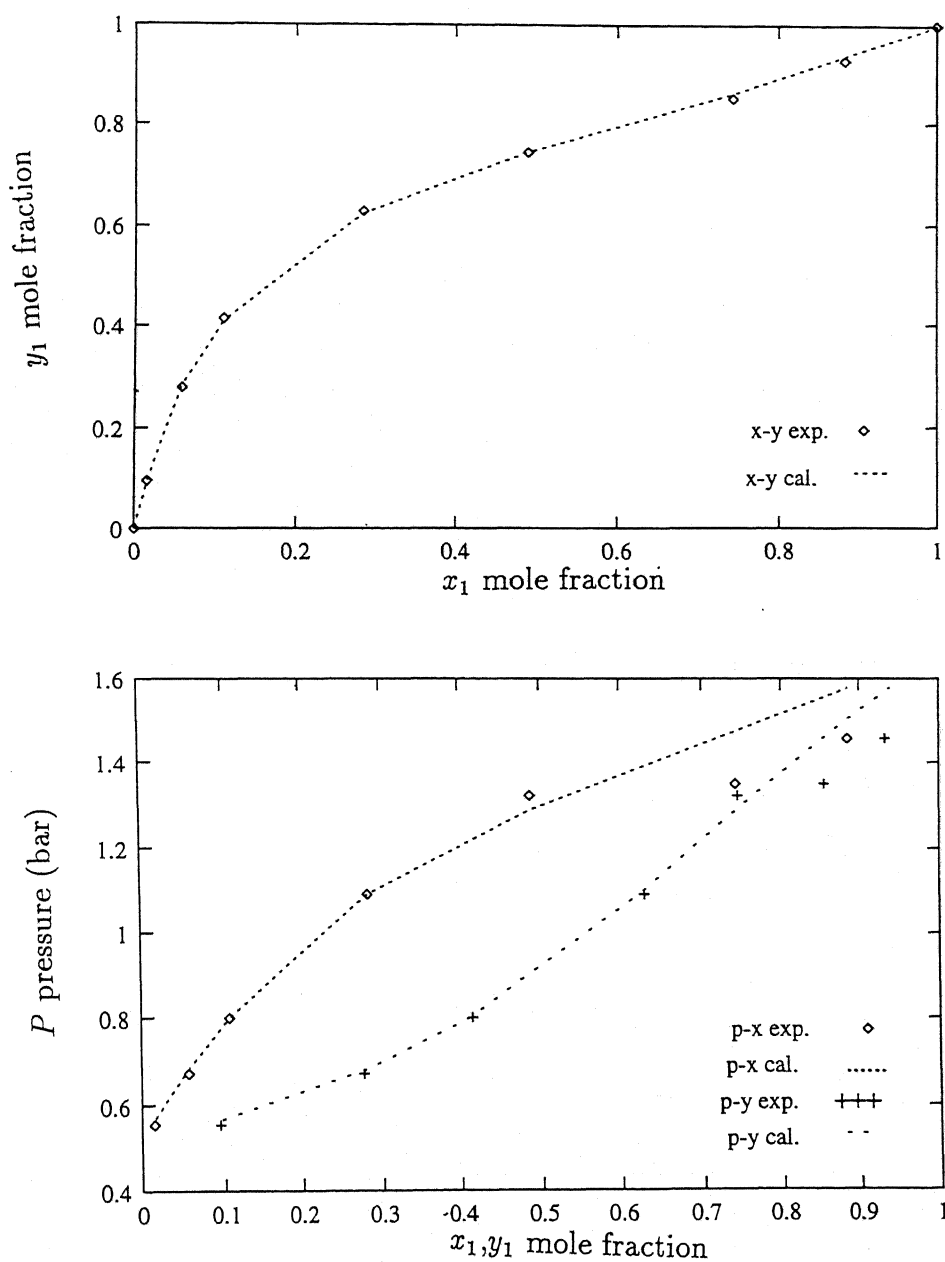


Figure 5.15: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for 1 – hexene – 1,4 – dioxane system at 353.15 K.

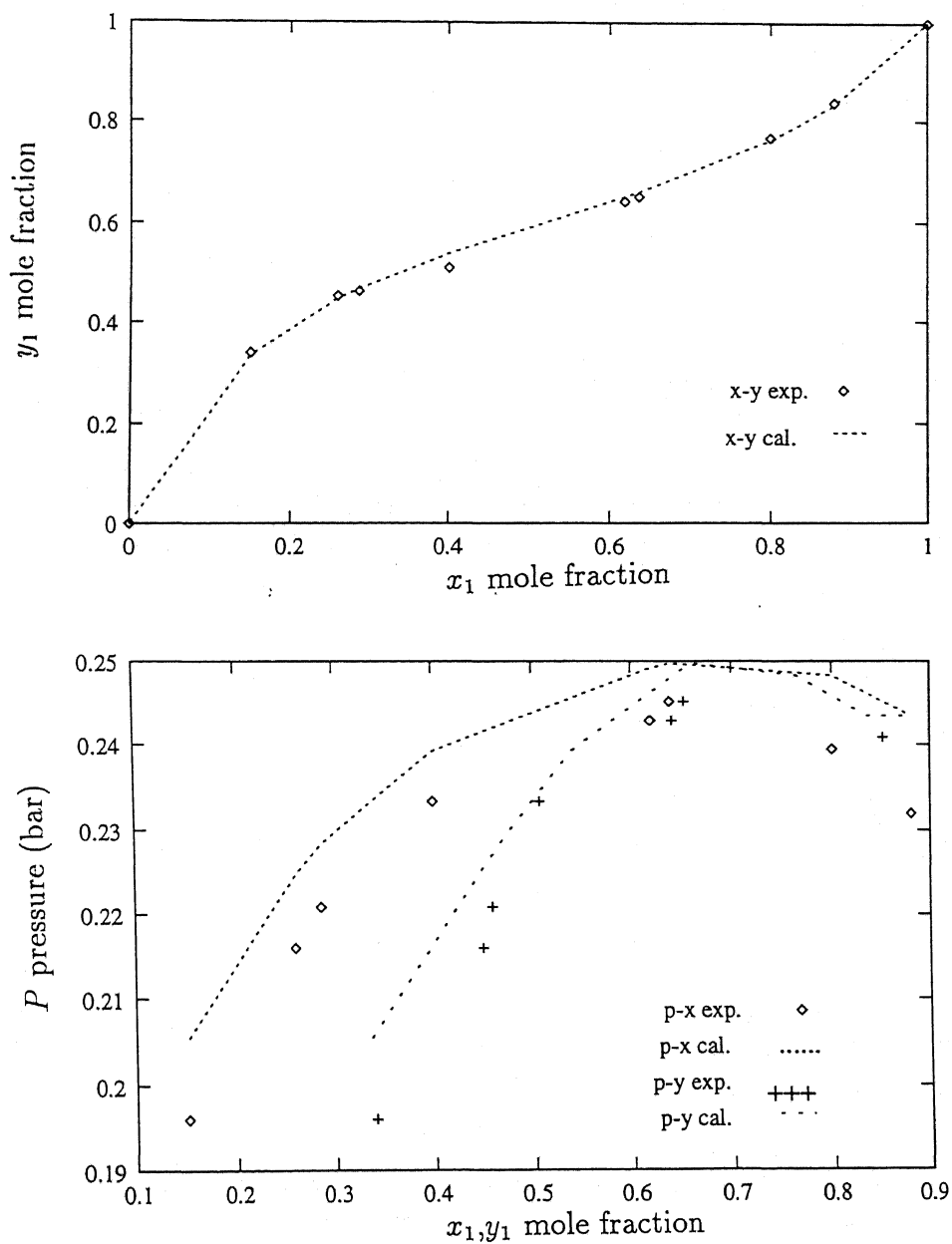


Figure 5.16: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *methanol* – *acetonitrile* system at 303.15 K.

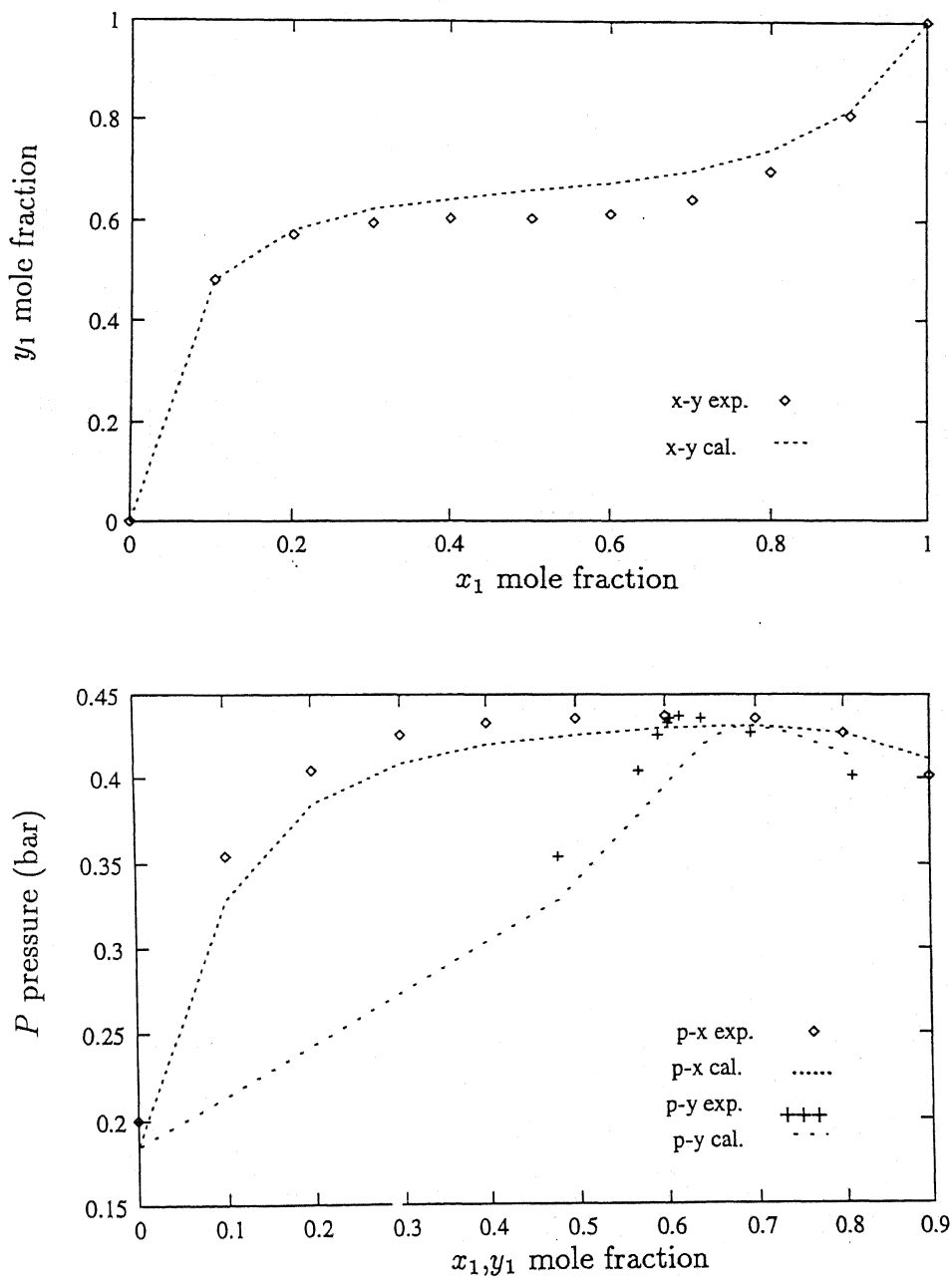


Figure 5.17: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *methanol* – *1,2 – dichloroethane* system at 313.15 K.

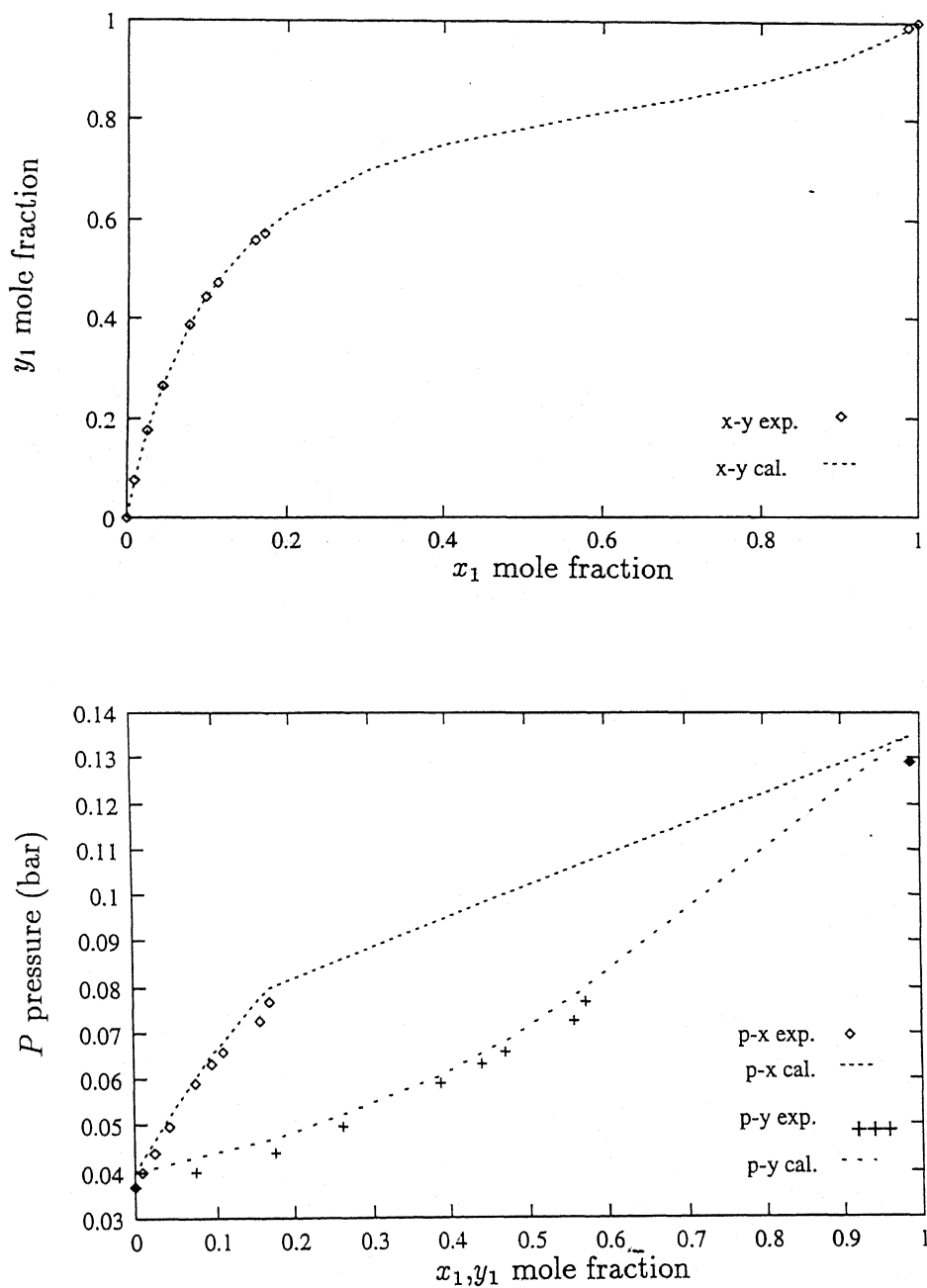


Figure 5.18: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *methanol* – 1,4 – *dioxane* system at 293.15 K.

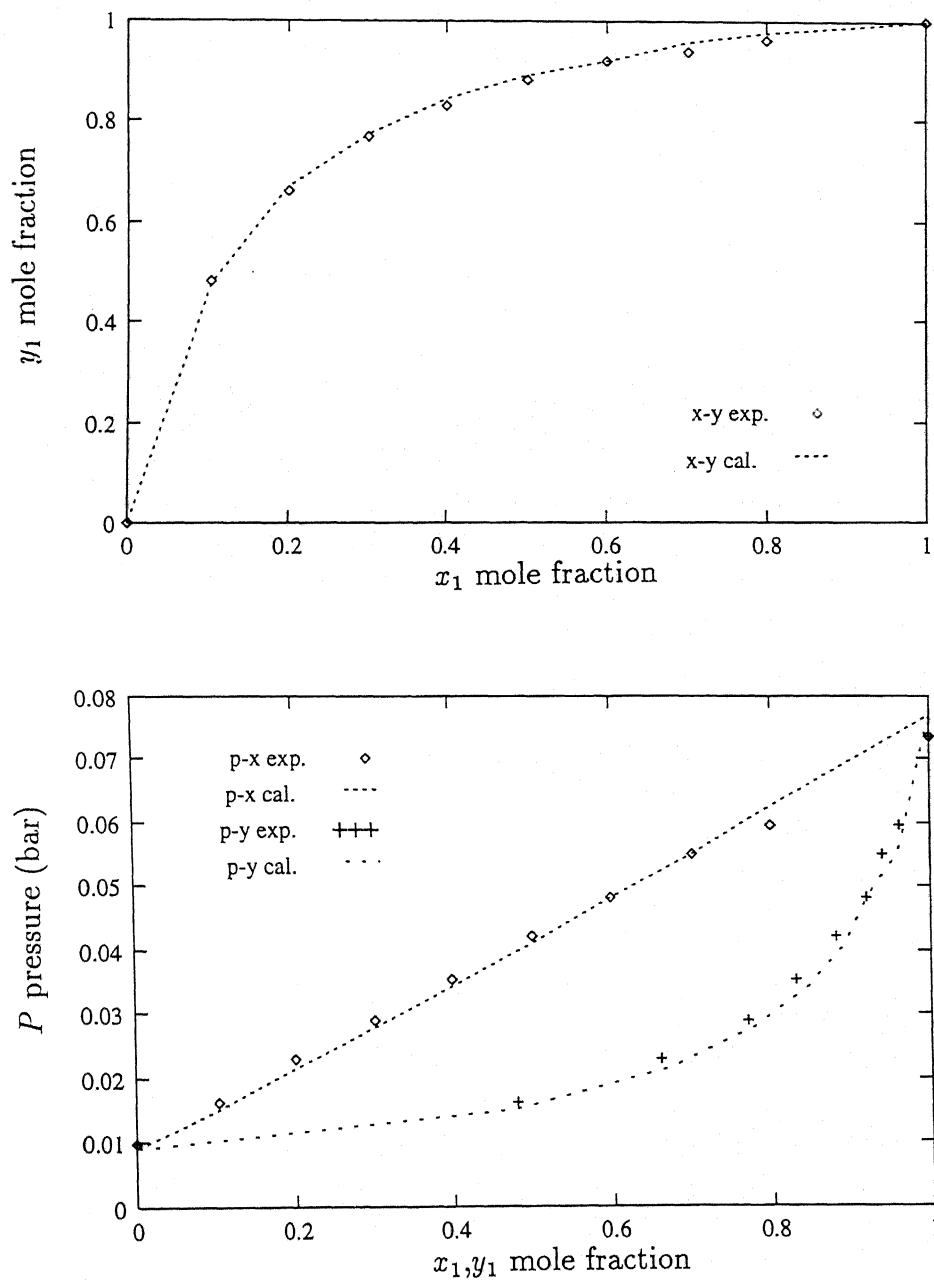


Figure 5.19: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *methanol* – 1 – *propanol* system at 283.15 K.

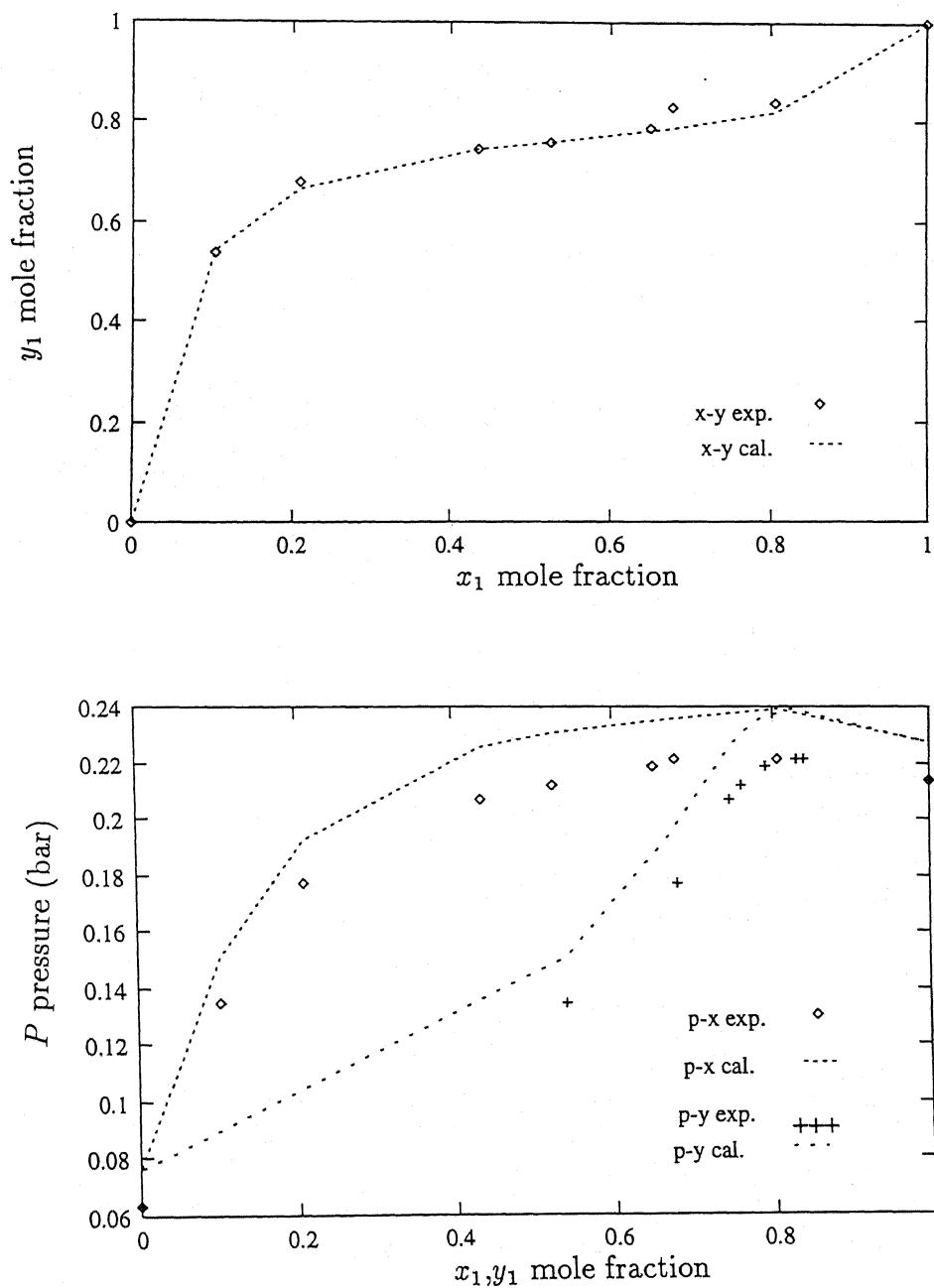


Figure 5.20: Comparison of experimental and calculated values of  $y_i$  and  $P$  from Wong-Sandler mixing rules for *methanol* – *nitromethane* system at 303.15 K.



# Chapter 6

## CONCLUSIONS

The applied thermodynamicists have been trying to replace the activity coefficient models for mixtures with equations of state; because of the following reasons.

- \* To avoid the use of standard states and hypothetical phase conditions.
- \* To have models which can be used at high pressures and close to a vapor-liquid critical point.
- \* To have models that cover a wide range of temperature and pressure with few parameters.

The only hinderance, for this is the lack of suitable mixing rules to obtain the equation of state parameters for mixtures.

In this work, we have used a theoretically correct mixing rule for a cubic equation of state (though the procedure is applicable to other equations of state as well), which applies to all mixtures. The unique feature of this mixing rule is that, while it is independent of density when combined with an equation of state, it converges to the activity coefficient model. This mixing rule provides a unified and consistent way of combining equations of state and excess free energy models to encompass mixtures that previously could only be described by one or the other. Since we have complete freedom in choosing the expression for  $A_{\infty}^E$ , this new mixing rule can be used to describe a wide variety of mixtures and phase behaviour. Because of the limited amount of time, this work is restricted to the study of binary systems only. In order to establish the present findings on a firm basis the same study can be continued to ternary systems and also to the systems that could not previously be described by equations of state.

According to the recent work of Orbey and Sandler [26], this new model has the flexibility of adding binary interaction parameters. These can be introduced in the form

$$\left[ b_{ij} - \frac{a_{ij}}{RT} \right] = \frac{1}{2}(b_{ii} + b_{jj})(1 - l_{ij}) - \frac{\sqrt{a_{ii}a_{jj}}}{RT}(1 - k_{ij}) \quad (6.1)$$

The Equation ( 6.1) has the advantage that when used with certain expressions for  $G_{\gamma}^{ex}$ , by variation of the parameters the mixing rule takes the form of van der Waals one-fluid mixing rule. Hence, by using this model, some binary pairs in a multicomponent mixture can be described by van der Waals one fluid mixing rule, while others are described by activity coefficient based mixing rules.

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